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MINERAL COMPOSITION OF GUMMITE*†

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ABSTRACT

The name gummite has been widely used for more than 100 years as a generic term to designate fine-grained yellow to orange-red alteration products of uraninite whose true identity is unknown. A study of about 100 specimens of gummite from world-wide localities has been made by *x*-ray, optical, and chemical methods. It proved possible to identify almost all of the specimens with already known uranium minerals.

Gummite typically occurs as an alteration product of uraninite crystals in pegmatite. Such specimens show a characteristic sequence of alteration products: (1) A central core of black or brownish-black uraninite. (2) A surrounding zone, yellow to orange-red, composed chiefly of hydrated lead uranyl oxides. This zone constitutes the traditional gummite. It is principally composed of fourmarierite, vandendriesscheite and two unidentified phases (Mineral *A* and Mineral *C*). Less common constituents are clarkeite, becquerelite, curite, and schoepite. (3) An outer silicate zone. This usually is dense with a greenish-yellow color and is composed of uranophane or beta-uranophane; it is sometimes soft and earthy with a straw-yellow to pale-brown color and is then usually composed of kasolite or an unidentified phase (Mineral *B*). Soddyite and sklodowskite occur rarely.

There are minor variations in the above general sequence. In some specimens the core may be orange-red gummite without residual uraninite or the original uraninite crystal may be wholly converted to silicates. Other specimens show clarkeite as the core, or an intermediate zone of clarkeite may form between the central uraninite and the orange-red zone of hydrated oxides. The uranyl carbonate rutherfordine has been observed as the outermost zone in some specimens, usually more or less admixed with uranyl silicates.

Chemically the formation of the minerals of the orange-red gummite zone at the expense of the original uraninite is characterized by oxidation of U^4 to U^6 and hydration. There is usually little or no addition of material other than H_2O at this stage, but leaching of U relative to Pb may be a factor. The Pb in the minerals of this zone is the original radiogenic lead of the uraninite. The outermost silicate zone is due to reaction of the hydrated oxides of the gummite zone with meteoric or possibly hydrothermal waters carrying silica and usually also calcium. The Pb may be removed at this stage, together with uranium in part, with the formation of uranophane, beta-uranophane, or soddyite, or it may be retained in part or entirely with the formation of Mineral *B* or kasolite. The Th and rare earths contained in the original uraninite usually are wholly removed during the formation of the silicates.

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There is also a further stage of alteration of the uraninite of pegmatites, in which the substance of the pseudomorphs is leached away and is either dispersed or redeposited nearby in cracks in the matrix. The uranium minerals that occur in this way are chiefly the phosphates meta-autunite, parsonsite, and phosphuranylite, and the silicates uranophane, beta-uranophane, kasolite, and Mineral B. The alteration of uraninite in vein or other non-pegmatitic deposits follows the same general sequence of alteration described, both on a hand specimen and geologic scale. In the presence of abundant sulfides, however, a different assemblage of secondary minerals is formed. This is characterized by the formation of zippeite, uranopile, johannite, and gypsum, and there may be extensive leaching of uranium in the ground waters.

HISTORY AND NOMENCLATURE OF GUMMITE

Gummite is a vague term that has been and is used in various ways. Probably its commonest present-day use is as a generic term for gumlike or dense fine-grained pseudomorphic alteration products of uraninite whose true identity is not known. The term ordinarily is employed in lack of any knowledge of the composition other than that uranium is a major constituent. It also has been applied, as in the 7th edition of Dana's System of Mineralogy, in a more restricted chemical sense to substances that are essentially hydrated oxides of uranium, whose true identity is unknown, that represent the final stages of oxidation and hydration of uraninite. George (1949) states that gummite is a generic term applied to the usually orange or orange-yellow alteration products of uraninite or pitchblende. Gummite is regarded by Hey (1950) as an indefinite generic term analogous to limonite and wad.

Gummite is also loosely used without regard either to the pseudomorphic nature of the material or to its chemical composition, provided usually that the material is orange-red to yellowish in color and dense in appearance, and the matter thus grades into the problem of unidentified uranium minerals in general. The color of the material commonly is orange-red, orange or yellow, but may be greenish yellow, brown, or other colors depending on the identity and, in part, the state of subdivision of the mineral or minerals present. A gumlike or resinous appearance was emphasized in the early descriptions and synonymy of this substance, but this feature has not been recognized as a necessary criterion.

The name gummite has not been used always in a generic sense. The first analyzed and clearly described gummite—the *hyacinthrothes Pechuran* of Freiesleben (1817) and Kersten (1832) from Johanngeorgenstadt, so-called in distinction from *schwarzes Pechuran*, or pitchblende, of which it was said to be an alteration—was said to be opaline and resembling amber in appearance. Kersten considered the substance to be a distinct species, and gave the formula as $\text{Ca}_3(\text{PO}_4)_2 \cdot 4\text{UO}_3 \cdot 9\text{H}_2\text{O}$. Later, a number of more or less similar ill-defined substances were described under various

given names in the belief that they were distinct species. Some of these substances appear to be essentially oxidized uraninite, others are hydrated oxidation products thereof, and many appear to have been mixtures with uranophane and other secondary uranium minerals. A few of these names have found their way into the synonymy of uraninite and others are included in the complex group of unidentified substances now called gummite. The name gummite itself was first introduced by J. D. Dana in 1868 as a species designation for an impure hydrated uranium oxide. He included in it the material of Kersten together with the Uran-gummi and Uranisches Gummi-Erz of Breithaupt (1930, 1847) and the Phosphor-Gummit of Hermann (1859). The pittinite of Hermann (1859) and eliasite of Haidinger (1852) were classed as a hydrated uranium oxide species (eliasite) separate from both uraninite and gummite, but it was remarked by Dana that the species may not be distinct from gummite. In 1883, Von Foullon made a detailed microscopic and chemical examination of gummite in the sense of Dana, including therein pittinite, eliasite, and the coracite of Whitney (1849) and Genth (1857), and sought to show that the substance was a definite species with the composition $(\text{Pb}, \text{Ca}, \text{Ba})\text{U}_3\text{SiO}_{12} \cdot 6\text{H}_2\text{O}$. Strunz (1949) accepts this view in part. He considers that gummite is principally a gel-like, pseudomorphous alteration product of uraninite with the formula given by Von Foullon, but certainly also in part a mixture of different cryptocrystalline uranium minerals. This particular matter is discussed further below—where it is shown from a re-examination of Von Foullon's original specimens that his formula represents a mechanical mixture of a lead uranyl oxide with a calcium uranyl silicate.

E. S. Dana in the 1892 edition of the *System of Mineralogy* placed gummite as a numbered species in the Uranate Group and stated that it is an alteration product of uraninite of doubtful composition, with the implication that further study would characterize it as a distinct species. It is difficult to see how this could be effected. Evidence is lacking which permits gummite in the sense of Dana either to be identified with or distinguished from any of the many known uranium minerals within the range of the chemical analyses and descriptions of gummite that have been reported, nor are type specimens available whose re-study would arbitrarily resolve the problem, as the name is not based on the description of a particular specimen but was applied to a pre-existing group of minerals thought but never shown to be identical. The present tendency to use gummite as a generic term is a recognition of these difficulties.

Gummite together with limonite and wad are modern examples of the great pocket terms that contained much of ancient mineralogy. Among the latter may be mentioned bole, misy, and especially schorl, which once

included even the rudely hexagonal columns of basaltic lava. Schorl and the others were largely resolved into their component species in the decades immediately preceding and following 1800, with the advance of chemistry and morphological crystallography in that period. In the present day, gummite and its analogues virtually disappear as units of description if x -ray diffraction, optical, and thermal methods are applied. The difficulties obtaining with gummite in the past were largely due to the very fine-grained and often admixed nature of the material. It is of interest to note that only one mineral, uranophane, of the dozen or so that have now been identified as constituents of gummite pseudomorphs was known at the time of the 1892 edition of Dana's *System of Mineralogy*.

In the present study, a collection of about 100 specimens of gummite from world-wide localities was examined by x -ray, optical, and chemical methods. All of the specimens were partial or complete pseudomorphs after uraninite, and had the color, dense appearance, and other characters attributed to gummite. It proved possible to identify almost all of the specimens with already known uranium minerals. Brief descriptions of these minerals are given in a later section of this paper. A few unidentified minerals, apparently new species, also were found. Three of these, Minerals A, B, and C, are briefly described in the present report.

The optical properties of the minerals that occur in gummite or that are associated therewith are summarized in Table 3, appended. The x -ray power spacing data for these minerals are given in Table 4, appended.

CHEMICAL ANALYSES OF GUMMITE

Nonexistence of Gummite as a Species

The reported chemical analyses of gummite are listed in Table 1. A brief discussion may be given here of these analyses in advance of a detailed description of the mineralogy of the substance. Von Foullon (1883) cited all of the older analyses given in Table 1. He accepted the SiO_2 and CaO , both present in fairly constant amounts, as essential constituents and derived the formula $(\text{Pb}, \text{Ca}, \text{Ba})\text{U}_3\text{SiO}_{12} \cdot 6\text{H}_2\text{O}$ for gummite.

The silica reported in the analyses of gummite, however, appears, from the observations of Genth (1879) and much other evidence, to be due to admixture principally of uranophane or beta-uranophane, $\text{CaO} \cdot 2\text{SiO}_2 \cdot 2\text{UO}_3 \cdot 6\text{H}_2\text{O}$, and Von Foullon's interpretation of gummite as a definite species with the formula cited never found general acceptance. The writer has examined all of Von Foullon's specimens through the courtesy of Dr. A. Schiener, Curator of Mineralogy of the Natural History Museum, Vienna. The North Carolina specimens had been originally obtained by Von Foullon from W. E. Hidden [1853-1918], an American mineralogist. Unfortunately, it is not possible to correlate particular specimens with

TABLE 1. CHEMICAL ANALYSES OF GUMMITE

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
CaO	3.19	3.04	2.05	0.90	4.54	3.87	3.09	2.26	1.37	0.48	6.00	2.1	10.36		1.64	tr.	1.10	4.60	3.80
MgO					0.85	tr.	2.20	0.55	0.12	0.27									
BaO	1.04	0.92	1.08	2.16			tr.												
PbO	5.51	4.69	5.57	5.28	5.04	3.92	4.62	2.51	14.93	20.15			1.66						
Fe ₂ O ₃	0.41	1.06		0.29	8.64	7.25	6.63	4.54				4.0	6.39	0.71	6.93	5.20	10.92	7.90	6.67
Al ₂ O ₃				0.53	0.86		1.17		0.14										
UO ₂	74.79	74.50	75.20	77.99	63.38	66.57	61.33	68.45	60.36	73.20	72.00	77.4	68.20	81.32	82.19	80.97	78.13	62.91	60.88
P ₂ O ₅				0.12			0.84				2.30				tr.	tr.		0.15	1.34
SiO ₂	5.03	5.04	4.63	1.97	4.92	4.96	5.13	5.00	3.81	0.61	4.26	1.4	2.80	8.20	3.80	3.04	2.50	13.00	15.25
H ₂ O	9.86	9.94	10.54	8.90	10.24	11.86	10.68	10.06	9.42	5.33	14.75	9.3	9.45	7.29	6.10	8.80	7.00	11.00	11.00
Rem.				2.51	1.92	0.74	3.61	5.87	9.41		0.05	6.0	0.15	1.67	0.40	2.96	0.05	0.87	0.25
Total	99.83	99.19	99.72	100.86	99.53	99.17	99.30	99.24	99.56	100.04	99.36	100.2	99.01	99.19	101.06	100.97	99.70	100.43	99.19

1. Orange red material. Mitchell County, North Carolina. Von Foulton (1883). Average of two analyses.
2. Orange red material. Mitchell County, North Carolina. Von Foulton (1883).
3. Orange red material. Flat Rock mine, Mitchell County, North Carolina. Gent (1879).
4. Orange red material. Wiseman's mine, Spruce Pine, Mitchell County, North Carolina. Ross, Henderson, and Posnjak (1931). Rem. is K_2O 0.86, Na_2O 0.51, ThO_2 and rare earths 1.06, insol. 0.08. Mineral C.
- 5, 6. "Eliasite." Joachimsthal, Bohemia. Von Foulton (1883) cites two additional very similar analyses. Rem. is Mn_2O_3 .
7. "Eliasite." Joachimsthal, Bohemia. Ragsky (1853). Rem. is FeO 1.09, CO_2 2.52.
8. "Pittitite." Joachimsthal, Bohemia. Hermann (1859). Rem. is Bi_2O_3 2.67, insol. 3.20.
9. Flame-scarlet material. Villeneuve, Quebec. Ellsworth (1930). Rem. is ThO_2 7.66, Ce_2O_3 0.14, Y_2O_3 1.61, CO_2 undet.
10. Brownish-yellow material. Kambove, Katanga. Schoep and de Leenherr (1937).
11. Hyacinth-red material. Johanngeorgenstadt, Saxony. Kersten (1832). Rem. is Mn_2O_3 .
12. Brownish-red material. Mitchell County, North Carolina. Analysis by R. Meyrowitz, U. S. Geological Survey, 1954. Rem. is Na_2O 1.1, UO_2 0.4, R_2O_3 (mostly Y and
13. Orange-red material. Luwishi, Katanga. Gillet analysis in Buttgenbach (1922). Sp. Gr. 5.08.
14. Gummite. Alto do Tibiri, Paraíba, Brazil. Rem. is UO_2 . Florencio (1951).
15. Orange material. La Chiquita mine, Sierra de Començingones, Córdoba, Argentina. Rem. is ThO_2 and rare earths. H_2O is loss on ignition. Chaudet analysis in Ahlfeld and Angelelli (1948).
16. Yellowish-orange material. Angel mine, Calamuchita, Córdoba, Argentina. Rem. is ThO_2 and rare earths 2.15, UO_2 0.81, H_2O is loss on ignition. Sp. Gr. 4.10. Chaudet analysis in Ahlfeld and Angelelli (1948).
17. Yellow material. Tigre mine, Sierra de Començingones, Córdoba, Argentina. Rem. is ThO_2 and rare earths 0.05. H_2O is loss on ignition. Sp. Gr. 4.20. Chaudet analysis in Ahlfeld and Angelelli (1948).
18. Light-brown material. Tigre mine, Sierra de Començingones, Córdoba, Argentina. Rem. is ThO_2 and rare earths. H_2O is loss on ignition. Chaudet analysis in Ahlfeld and Angelelli (1948).
19. Yellow material. Tigre mine, Sierra de Començingones, Córdoba, Argentina. Rem. is ThO_2 and rare earths. H_2O is loss on ignition. Chaudet analysis in Ahlfeld and Angelelli (1948).

the analyses cited by Von Foullon. *X*-ray and optical studies of his specimens from Mitchell County, North Carolina, including the materials of analyses 1 and 2 (Table 1), although these could not be specifically identified, show that they are variable mixtures of uranophane with vandendriesscheite or an unidentified lead uranyl oxide. Specimens of identical appearance from Mitchell County contained in other collections also were found to be mixtures of uranophane or beta-uranophane, with vandendriesscheite and, in some specimens, clarkeite, fourmarierite, and unidentified lead uranyl oxides. A sample of the gummite from Mitchell County analyzed by Ross, Henderson, and Posnjak (1931), cited in column 4 of Table 1, and supplied for examination by Dr. George Switzer of the U. S. National Museum, was found on *x*-ray and optical study to be an unidentified phase, Mineral C. This mineral is closely associated with uranophane, and the analyzed sample is described as of questionable homogeneity. A new analysis of a brownish-red gummite from Mitchell County is cited in column 12 of Table 1. This material also gave the *x*-ray pattern of Mineral C.

If the analyses of the material from Mitchell County cited in columns 1, 2, and 3 of Table 1 are recalculated after deduction of the SiO_2 as uranophane, $\text{CaO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$, the remaining substance is seen from the data of Table 2 to have virtually the composition of vandendriesscheite. Analyses 1 and 2 have a slight excess of CaO over the requirements of the SiO_2 for uranophane, and analysis 3 a slight deficiency (3.19, 3.04, 2.05 present; 2.35, 2.35, 2.16 required). In the analyses as recalculated, all of the CaO and SiO_2 was deducted together with the amounts of UO_3 and H_2O required by the SiO_2 present. The Ba present in these analyses undoubtedly substitutes for Pb.

Analysis 11 by Kersten (1832) of the "hyacinthrothes Pechuran" from Johannegeorgenstadt is rather similar to those just discussed if it is assumed, as was suggested by Von Foullon (1883), that much of the Ca reported actually is Pb. Analyses 5, 6, and 7 of eliasite and pittinite from Joachimsthal apparently represent mixtures of limonite and uranophane with a lead uranyl oxide. Type specimens of eliasite and pittinite are not available for examination. However, one specimen from Joachimsthal of uraninite altered to orange-colored gummite was found here to be composed of fourmarierite and uranophane and another was composed of vandendriesscheite. Analysis 10 is close to curite in composition. Analysis 9 was made on admittedly inhomogenous material containing perhaps 25 per cent of another mineral that appears from its description to be uranophane. The deep color and high lead content of this material suggests that the gummite component was perhaps curite. Rigal (1938) cites a partial analysis of a very impure orange gummite from Argentina

that apparently contains about 5 per cent PbO and 80 per cent UO_3 . Chaudhuri (1944) found radiometrically that an orange-yellow gummite from Rajputana contained about 71 per cent UO_3 and 0.8 per cent ThO_2 . Krishnan (1948) cites partial analyses of impure gummite from Rajputana. Florencio (1951) has reported an analysis of a gummite pseudomorph after uraninite from Alto do Tibiri, Paraiba, Brazil, that apparently consists of a hydrated uranyl silicate, possible soddyite. The analysis is reported in column 14, Table 1. Five analyses of gummite and uranium ochre from Córdoba province, Argentina, reported by Ahlfeld and Angelelli (1948) are cited in columns 15 to 19, Table 1. The material

TABLE 2. RECALCULATED ANALYSIS OF GUMMITE

	1	2	3	4	5	6
BaO	1.7	1.5	1.6			
PbO	8.8	7.7	8.3	9.14	15.31	22.10
UO_3	81.0	82.0	80.5	82.00	78.51	75.52
H_2O	8.5	8.8	9.6	8.86	6.18	2.38
Total	100.0	100.0	100.0	100.00	100.00	100.00

1. Mitchell County, North Carolina. Von Fouchon (1883). Analysis 1, Table 1, recalculated after deducting uranophane and Fe_2O_3 .
2. Mitchell County, North Carolina. Von Fouchon (1883). Analysis 2, Table 1, recalculated after deducting uranophane and Fe_2O_3 .
3. Mitchell County, North Carolina. Genth (1879). Analysis 3, Table 1, recalculated after deducting uranophane and Al_2O_3 , P_2O_5 .
4. Vandendriesscheite. Theoretical composition, $\text{PbO} \cdot 7\text{UO}_3 \cdot 12\text{H}_2\text{O}$.
5. Fourmarierite. Theoretical composition, $\text{PbO} \cdot 4\text{UO}_3 \cdot 7\text{H}_2\text{O}$.
6. Curite. Theoretical composition, $3\text{PbO} \cdot 8\text{UO}_3 \cdot 4\text{H}_2\text{O}$.

occurs as alteration products of uraninite in pegmatites. The analyses resemble those of gummite in general, and apparently are mixtures with uranophane and, in analysis 19, possibly also quartz or other insoluble material. The presence of uranophane (?) is noted in material from Angel mine (analysis 16, which lacks CaO), and this mineral was identified in specimens of gummite from Córdoba examined by the writer.

The x-ray and chemical evidence indicates that the gummite from Mitchell County, North Carolina, is not a definite compound containing essential Ca and Si, as was believed by Von Fouchon, but is a mixture of a calcium uranyl silicate, uranophane, with a lead uranyl oxide, usually vandendriesscheite. This view is strongly supported by the fact that similar specimens of gummite, from localities over the world, are found to be composed of lead uranyl oxides, usually vandendriesscheite,

Mineral *A*, Mineral *C*, or fourmarierite, admixed or associated with the silicates uranophane, beta-uranophane, kasolite, or Mineral *B*.

SEQUENTIAL ALTERATION OF URANINITE

Mineralogy

Gummite pseudomorphs after uraninite crystals show a very characteristic sequence of alteration products that has long been recognized. Brief descriptions have been given by Kerr (1877), Genth (1879), Hidden (1881), Von Foulton (1883), Hoffman (1901), Tipper (1919), Schoep (1921), Buttgenbach (1922), Hacquaert (1927), Ellsworth (1930), Ross, Henderson, and Posnjak (1931), Yagoda (1946), Sarkar and Sen (1946), Krishnan (1948), Bakken, Gleditsch, and Pappas (1948), and Page (1950). The best examples are afforded by the uraninite crystals found in pegmatites, but the same principles apply to uraninite in all of its occurrences. When a typical, partly altered crystal is broken across, one finds: (1) A veined or embayed central core of uraninite. The color may be black or, in relatively highly oxidized material, greenish black, brownish black, or dark brown. (2) A surrounding zone of orange-red, orange, brownish-red, brown, or yellow material that constitutes the traditional gummite. This material is dense in structure, although microscopically crystalline, and ranges from vitreous or gumlike to dull and earthy in appearance. In composition it consists chiefly of hydrated uranyl oxides, often containing considerable amounts of essential lead together with minor amounts of calcium and barium. The commonest mineral constituents are vandendriesscheite, fourmarierite, Mineral *A*, and Mineral *C*. Curite, becquerelite, and schoepite also have been identified, and several unidentified minerals have been found. (3) An outer zone of uranyl silicates. This zone generally is hard, dense, and microcrystalline with a greenish-yellow color and vitreous luster but may be soft and earthy with a straw-yellow color and dull luster. The hard, vitreous material often faithfully preserves the minute surface details of the original uraninite crystals. The silicate zone grades into the hydrated oxide zone and has been derived from it. The principal minerals of this zone are uranophane, beta-uranophane, and kasolite. Mineral *B*, soddyite, sklodowskite, and several unidentified minerals also occur.

This sequence may vary considerably in detail. Thus, the original uraninite may be completely oxidized leaving a pseudomorph of orange gummite, with a more or less thick rind of uranium silicate, or the pseudomorph may consist largely or entirely of uranium silicate. Further, additional more or less well marked zones may be present. Specimens from a few localities were found to have an irregular outer zone of the uranyl carbonate rutherfordine which graded inwardly into orange-red

gummite. Complete pseudomorphs of rutherfordine also were observed. Other specimens showed brown clarkeite as the core, or an intermediate zone of clarkeite was present between the uraninite core and the outer gummite and silicate zones. The gummite zone itself may be irregularly mottled or veined in orange-red, red, or yellow colors due to admixture of various minerals.

There is also a further stage of alteration of the uraninite of pegmatites, in which the substance of the pseudomorphs is leached away and is dispersed or redeposited in cracks in the matrix in the immediate neighborhood of the pseudomorphs. The secondary uranium minerals that occur in this way are chiefly the phosphates meta-autunite, parsonsite, and phosphuranylite and the silicates uranophane, beta-uranophane, kasolite, and Mineral B.

The alteration sequence just described seems to take place at essentially atmospheric conditions through the agency of meteoric waters. It also has been considered, apparently first by Ross, Henderson, and Posnjak (1931), that the alteration of the uraninite of pegmatites to gummite and silicates took place during the late hydrothermal stage of pegmatite formation. It may be noted in this connection, however, that the uraninite of various nonpegmatitic deposits, including the Colorado Plateau region, Katanga, Great Bear Lake, and Joachimsthal, undergoes an identical sequence of alterations under what are clearly weathering conditions. George (1949) also points out that in the uraninite vein deposits of Portugal, uranophane and beta-uranophane are much more abundant toward the surface and are there associated with typical supergene uranium minerals such as autunite and torbernite. According to Websky (1853, 1859), uranophane at its type locality, Kupferberg, Silesia, is formed by atmospheric influences on primary uraninite in the copper veins. Hayden (1914) remarks that uranium ocher (gummite) is common at the surface of pegmatites in the Gaya district, India, and passes into pure uraninite in depth (where a nodule 36 pounds in weight was found). This also is true in the New England pegmatites. The occurrence of uraninite in pegmatites has been discussed by Page (1950) and Quensel (1940). Lang (1952) mentions 27 occurrences of gummite in Canada, mostly in pegmatites.

The sequence of alteration of uraninite on a single-crystal scale is broadly paralleled by the alteration of vein deposits of uraninite on a geologic scale. Thus, in the Katanga deposits the uraninite alters first to hydrated uranyl oxides or lead uranyl oxides, principally becquerelite, schoepite, vandendriesscheite, and fourmarierite. These minerals occur chiefly as crystalline crusts and masses, involving deposition from solution, and are not pseudomorphous alteration products. Pseudomorphs

also occur but are rare. The very rare secondary mineral ianthinite, a hydrated oxide of quadrivalent uranium, is formed earlier than these hexivalent oxides and occurs as crystals in veinlets penetrating uraninite. The formation of the hydrated uranyl oxides is accompanied and followed by the deposition of hydrated uranyl phosphates and silicates, generally containing copper, calcium, magnesium, or lead in addition to uranium. These have formed as crusts and masses chiefly by the action of meteoric waters carrying Cu, Ca, Mg, phosphate, and silica on the earlier formed hydrated oxides. The phosphate apparently has been derived by meteoric waters from the country rock. Unfortunately there is no detailed account of the paragenesis of the secondary uranium minerals at Katanga in the available literature. Brief accounts are given by Robert (1940), Katz and Rabinowitch (1951), Everhart (1951), Thoreau and Terdonck (1933, 1935), Bain (1950), and Kohl (1954), and scattered remarks are found in the literature descriptive of individual species. The above sequence, recognized in the literature, is confirmed by the examination of Museum specimens. Uraninite deposits rich in sulfides generally alter directly to the sulfates zippeite, uranopilite, and johannite, and probably much of the uranium is lost in the meteoric circulation if the water is acid. The uraninite deposits of the Canadian shield, as at Great Bear Lake and Lake Athabaska, show only a very slight supergene alteration, chiefly to hydrated uranyl oxides and silicates.

The uraninite of the sandstone-type deposits of the Colorado Plateau generally is intimately associated with montroseite and other primary low-valence vanadium minerals and on oxidation passes to carnotite, tyuyamunite or other secondary uranyl vanadates. In a few instances, however, as at the Monument No. 2 mine, Monument Valley, Arizona, and the Delta mine, San Rafael Swell, Utah, uraninite is found superficially altered to becquerelite and schoepite; the lead-bearing oxides fourmarierite and vandendriesscheite are lacking except in traces. Lead-bearing secondary uranium minerals, including kasolite, curite, parsonsite, dewindtite, renardite and dumontite, are lacking in general in the Plateau deposits, in contrast to their abundant occurrence in the Belgian Congo. This is owing to the general absence of lead-containing minerals such as galena in the unoxidized ores and to the low content of radiogenic lead in the uraninite of the Plateau deposits.

Chemistry

The chemistry of the sequential alteration of uraninite crystals offers a number of interesting problems. In the initial stage of alteration, the uraninite itself oxidizes over a range of composition without destruction of its crystal structure. In this, it is well established that valence com-

pensation for the serial oxidation of U^4 to U^6 is effected by a coupled entrance of oxygen into the vacant eight-coordinated positions of the structure. The extent of oxidation that is possible before the structure breaks down is not known. It appears to be in the neighborhood of $UO_{2.3}$ (see Katz and Rabinowitch, 1951) or $UO_{2.6}$ (see Brooker and Nuffield, 1952). The effect that the presence of Pb, Th, and rare earths in substitution for U has on the extent of the oxidation is not known. A similar mechanism of compositional variation is known in other substances isostructural with UO_2 , including the substitution of Y, Th, or U^4 for Ca in CaF_2 ; La for Sr in SrF_2 ; and Bi for Pb in PbF_2 . In these instances F enters the interstitial positions to effect valence compensation. It also has been suggested that the content of U^6 in natural uraninite is due to an auto-oxidation involving radioactive decay processes independent of the environment (Ellsworth, 1925, and Khlopin, 1938). Attempts based on this assumption to use the U^4/U^6 ratio for age calculations have been unsatisfactory. It seems likely that the oxidation is a forerunner of the hydration and chemical reaction with traversing, oxidizing solutions that ultimately convert the uraninite completely into the minerals of the gummite and silicate zones. It is of interest to note that neither U_3O_8 nor the tetragonal polymorph of partly oxidized uraninite ($\sim UO_{2.4}$) have been found in nature, although both are stable, well-known compounds easily formed by the oxidation of UO_2 .

In the second stage of alteration, the uraninite is destroyed and its constituents are reorganized into the hydrated lead uranyl oxide minerals of the orange-red gummite zone. The change involves complete oxidation of the uranium to U^6 and hydration, without significant gain of material other than water, but possibly with leaching of uranium in part relative to lead. It is apparent from the examination of many specimens that the parent uraninite does not have to be oxidized to its limiting content of U^6 in the UO_2 structure-type before it converts to these new phases, although it may alter more readily if it is relatively highly oxidized. The radiogenic lead of the original uraninite seems to be wholly retained in the new minerals formed at this stage. The particular mineral or minerals formed here, whether schoepite or becquerelite (little or no lead), vanderdriesscheite (9.1 per cent lead), fourmarierite (15.3 per cent lead), or curite (22.1 per cent lead) presumably reflects the amount of radiogenic lead available in the original uraninite. Leaching of uranium relative to lead is an added factor. No zoning of the minerals of this stage in point of lead content has been observed. The amount of radiogenic lead in uraninite ordinarily runs from about 3 to 10 weight per cent PbO, but as much as 19 per cent PbO has been reported. Curite, with the highest content of Pb of the secondary hydrated uranyl oxides, is very rare in gum-

mite alteration pseudomorphs. Schoepite and becquerelite, with little or no lead, also are very rare. At Katanga, its principal locality, curite is formed chiefly by direct crystallization from lead-containing solutions and is relatively late-formed in the paragenesis. The question of the valence state of the Pb present in uraninite and in some of the red-colored secondary oxides requires further investigation. It always is reported as Pb^2 by analysts. Wasserstein (1954), in his work on the determination of age by unit-cell measurements of uraninite, assumes the lead to be present as Pb^4 .

In the third stage of alteration, the hydrated oxides of the gummite zone react chemically with traversing solutions, ordinarily of the meteoric circulation but possibly at times of hydrothermal origin, with the formation of uranyl silicates and, occasionally, of the uranyl carbonate rutherfordine. Calcium ordinarily is added at this time, in addition to silica and water, giving rise to the characteristic minerals of this zone, uranophane, beta-uranophane, and Mineral *B*. Soddyite, a uranyl silicate lacking Pb, Ca, or other cations, also may form at this stage but is rare. Lead, retained during the gummite stage, ordinarily is completely lost during the formation of the silicates. Sometimes it is retained and concentrated relative to uranium with the formation of kasolite, with 37.5 per cent PbO , and Pb also is sometimes present in solid solution in Mineral *B*. Uranium, present in the silicates of this stage in amounts between 49 and 67 per cent UO_3 , apparently must be lost in part since the alteration commonly takes place without appreciable change in volume (pseudomorphic).

The history of the thorium and the rare earths contained in the original uraninite is not entirely clear. Analyses 4, 9, 12, and 15 to 19 of Table 1 indicate that these elements are retained at least in part in the minerals of the gummite zone. This also is indicated by a spectrographic study of zoned pseudomorphs made for the writer by Mr. H. C. Harrison. This study further showed that the thorium and rare earths tend to be leached out during the silicate stage of alteration. An analysis of uranophane cited beyond, however, indicates that thorium and rare earths may be retained in small part in the silicate stage, but these elements are not found in most analyses of uranophane and beta-uranophane. The studies made of changes in the ratios of uranium, thorium, and lead during the oxidation of uraninite, in connection with the determination of geologic age by the U, Th/Pb method, indicate that thorium tends to decrease and lead to increase relative to uranium as alteration proceeds. [See Bakken, Gleditsch, and Pappas (1948), Gleditsch and Bakken (1937), Bakken and Gleditsch (1938), Alter and Kipp (1937), Hecht (1931), and Hecht and Kroupa (1936).] These observations apply to uraninite in the

initial stages of alteration. Uraninite that has passed into the gummite stage of alteration is worthless for age determination work. Føyn (1937) has described experiments on the leaching of uraninite in water in closed tubes at 190° C. Yagoda (1945) describes the occurrence of radiocolloid aggregates in gummite and gives a color photograph of a gummite specimen. The radiocolloids apparently owe their origin to the leaching and local reprecipitation of radiogenic radium as radium sulfate, which has since largely decayed to $\text{Pb}^{206}\text{SO}_4$.

Clarkeite contains sodium and calcium as essential constituents, together with lead, and occurs in the inner part of some uraninite pseudomorphs in pegmatites. The writer inclines to the view of Ross, Henderson, and Posnjak (1931) that the clarkeite was formed by reaction of the uraninite with late pegmatitic hydrothermal solutions containing alkalis. The outer gummite and silicate zones of these pseudomorphs probably were formed much later by meteoric solutions.

DESCRIPTION OF MINERALS PRESENT IN GUMMITE

Becquerelite, $7\text{UO}_3 \cdot 11\text{H}_2\text{O}$ (?)

Becquerelite was not identified as a constituent of the gummite specimens examined in the present study. It has been reported by Steinkuhler (1923) and Hacquaert (1927) in uraninite pseudomorphs from Katanga. The mineral ordinarily occurs at this locality not as an alteration product but as drusy crusts and aggregates that have been deposited directly from solution in the supergene zone. It was observed as a direct alteration product of massive uraninite, however, in specimens from the Monument No. 2 mine, Apache County, Arizona, the Delta mine, San Rafael Swell, Utah, and Lake Athabaska, Canada. The rarity of becquerelite in gummite is rather surprising, especially since the mineral apparently can contain lead in solid solution. Schoep (1936) describes specimens from Katanga showing a central core of uraninite that has altered first to becquerelite and orange fourmarierite and later to green vandenbrandeite and cuprosklodowskite. Scheerer (1847) described a uraninite crystal from a pegmatite in Norway that had been altered to a pale yellow hydrated uranyl oxide, possibly becquerelite or schoepite.

Beta-uranophane, $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$

Beta-uranophane, the monoclinic polymorph of uranophane, was found in a few occurrences as the chief constituent of the outer, silicate zone of alteration. In these occurrences the mineral is identical in color and general appearance with uranophane (which see); it is best distinguished by optical and x-ray tests. Beta-uranophane has inclined extinction and relatively high indices of refraction (Table 3). Steinocher and

Nováček (1939) note that beta-uranophane may convert to uranophane when finely crushed, so that care must be taken in preparing samples for x-ray or optical study. In gummite pseudomorphs, beta-uranophane characteristically has a yellowish-green color sometimes inclining to lemon yellow. Dense material is slightly translucent and has a weak vitreous to waxy-vitreous luster. Like uranophane, the mineral also occurs as soft, rather porous aggregates of a dull or earthy luster and then inclines to straw yellow and brownish-yellow shades of color. This soft material seems to be a product of leaching of the dense, vitreous pseudomorphs. Under the microscope the mineral appears as matted aggregates of fibers, often minute in size and distorted, and accurate optical measurements are difficult to obtain. Beta-uranophane was identified in material from the following localities: various pegmatites in the Spruce Pine district, Mitchell County, North Carolina; Newry, Maine; the Ruggles pegmatite, Grafton Center, and the Palermo pegmatite, North Groton, New Hampshire; Easton, Pennsylvania; Rajputana, India. It was also found as crusts of acicular crystals associated with altering uraninite at Theano Point, Lake Superior, Canada, and Wölsendorf, Bavaria.



Clarkeite was identified in a number of specimens from the Spruce Pine pegmatite district, North Carolina—the type locality for the mineral. It also was found at a new locality, the Ajmer district, Rajputana, India. The composition and properties of clarkite have been recently described by Gruner (1954) and by Frondel and Meyrowitz (1956). Clarkeite occurs as a direct alteration of uraninite. It is earlier formed than the minerals of the orange-red gummite zone and may alter to them. It differs from these minerals in its dark-brown or mahogany-brown color, and in containing Na and Ca in addition to Pb. It occurs as dense, fine-grained aggregates. The indices of refraction are high, near those of curite, and vary considerably with variation in the ratio of Na, Ca, and Pb (Table 3). A positive identification is best made by x-ray means (Table 4). The mineral also resembles the brownish-black, relatively highly oxidized types of uraninite. Clarkeite has been said to occur in reddish-brown gummite at the Ruggles pegmatite, Grafton Center, New Hampshire, but it was not observed in specimens from this locality examined in the present study.



Curite was not identified with certainty in any of the gummite pseudomorphs here examined. It may have been admixed in very small amounts

in some of the fourmarierite pseudomorphs. In one instance an x -ray pattern very close to that of curite was obtained from a deep orange-red gummite from Mitchell County, North Carolina, but the indices of refraction were much too low to confirm the identification. The orange-red to red color of many gummite specimens is not due to curite, as has been suspected in the past, but chiefly to fourmarierite and in part to vandendriesscheite. Curite pseudomorphs after uraninite crystals from Katanga have been described by Vernadsky and Chamie (1924), Van Aubele (1927), Schoep (1930), and Hacquaert (1927). Schoep and De Leenheer (1937) found that certain colloform crusts from Katanga, termed gummite by them, were composed of curite (analysis 10, Table 1). Their belief that all gummite is composed of curite is incorrect. A transparent, isotropic substance with a bright-scarlet color found here as an alteration product of uraninite from Fone, Gjerstad, Norway, may be an amorphous gel form of curite. It has an index of refraction slightly over 2, and did not give an x -ray diffraction pattern. A flame-scarlet alteration product of uraninite from Villeneuve, Quebec, analyzed by Ellsworth (1930) and cited in Table 1, might contain curite.

Fourmarierite, $\text{PbO} \cdot 4\text{UO}_3 \cdot 7\text{H}_2\text{O}$ (?)

Chemically, it is known from the reported analyses (Table 1) and from numerous spectrographic analyses made during the present study, that the minerals of the gummite zone of alteration are essentially hydrated oxides of uranium and lead. Barium, calcium, thorium, and alkalis often are also present in significant amounts in addition to lead. For practical purposes of identification, the minerals that fall into this general region of composition may be divided into two groups. The first group, comprising curite, clarkeite, becquerelite, billietite, and Mineral A, are relatively easy to identify in the present connection because their x -ray patterns are distinctive and their optical and other properties are also diagnostic. The second group, comprising fourmarierite, vandendriesscheite, schoepite, Mineral C, masuyite, and richetite, are difficult to identify. The x -ray powder patterns of all of these substances are very similar, and in the case of faint or diffuse patterns or of mutual admixture a positive discrimination becomes difficult or impossible by this method. In this case, the optical properties are of aid: schoepite without lead has much lower indices of refraction than the others, with $\gamma = 1.74$; vandendriesscheite and Mineral C have indices usually in the range 1.76–1.85; fourmarierite has higher indices, between 1.84 and 1.96 for the most part; the problematic mineral richetite is said to have β and γ from 2.00 to 2.07; masuyite has α 1.785, β 1.906, γ 1.917 according to one description and β 2.11, γ 2.15 according to another. Complete optical descriptions

are given in Table 3. In the present study, the standard x -ray patterns employed were obtained from type analyzed specimens of these minerals (with the exception of richetite, for which data and specimens are lacking). The x -ray pattern of masuyite is virtually identical with that of vandendriesscheite. The identification of these minerals in gummite was regarded as certain only if both the optical properties and the x -ray pattern answered the standard description. If, as was often the case, the optical properties were divergent or the optical properties answered the description and the x -ray pattern was diffuse and ambiguous, the identification was regarded as tentative. This procedure is not wholly satisfactory, as there are many uncertainties about the mutual relations of the minerals here classed together. Thus it is an open question whether the composition of these minerals is fixed, or whether there is a partial or complete variation in composition in point of lead content, with attendant variation in the x -ray pattern or optics, between some or all of them. Further, it is not known how the presence of barium or calcium in solid solution for lead affects the x -ray and optical constants. This is an important factor in the case of fourmarierite and vandendriesscheite at least. The barium and calcium analogues of fourmarierite have been synthesized.¹ They are isostructural with fourmarierite, and complete series probably extend between all three members. The barium uranyl oxide billietite was not identified in gummite, but it was observed as sharp crystals coating cracks in a fourmarierite pseudomorph after uraninite from Katanga. In the latter specimen the complete sequence of deposition was uraninite (core), fourmarierite, billietite, uranophane, torbernite.

Fourmarierite was identified in gummite from the following localities: Wölsendorf, Bavaria; Tvedestrand, Norway; as an alteration of pitchblende from an unstated locality in Bohemia, probably Joachimsthal; Bisundi, Rajputana, India; the Spruce Pine district, Mitchell County, North Carolina; Newry, Maine; the Katanga district, Belgian Congo; Mica Lakes area, Hahns Peak, Colorado. It also was found as thin colloform crusts on altering uraninite from Great Bear Lake, Canada. Some of the material from these localities had indices of refraction slightly higher than those reported in the literature, with gamma 1.95–1.97. Fourmarierite was doubtfully identified as a minor constituent of gummite from a number of localities, including Morogoro, Tanganyika; Rajputana, India; the Palermo and Ruggles pegmatites in New Hampshire; Pamplonita, Colombia (with γ a little over 2); the Ingersoll mine, Pennington County, South Dakota; Bathurst, Lanark County, Ontario;

¹ By Miss Eleanor R. Berman, Department of Mineralogy, Harvard University, 1954.

Wilberforce, Cardiff Township, Ontario. The mineral occurs as dense, microcrystalline aggregates, and the color is orange red. The color is lighter than that of curite. There is no question but that the indices of refraction of the mineral vary by at least 0.04 due to variation in composition, presumably the substitution of Ba and Ca for Pb.

Sarkar and Sen (1946) made an x-ray powder study of an orange-yellow gummite from Rajputana, India, which encased a residual of uraninite and was in turn surrounded by lemon-yellow uranophane. They concluded that the mineral was gummite (which they accept as a species name) from the near agreement of their d -spacings with the data given by Ross, Henderson, and Posnjak (1931) for an unanalyzed specimen of gummite (in the broad sense) from Mitchell County, North Carolina. This pattern is of the fourmarierite type but cannot be more closely identified. The optical properties given by Ross, Henderson, and Posnjak (α 1.742, β 1.762, γ 1.776, $2V$ 60° , $r < v$) differ from those of fourmarierite and vandendriesscheite but may represent Mineral C. Clarkeite and fourmarierite(?) were recognized in gummite specimens from Rajputana during the present study. Two partial analyses of impure gummite from Rajputana cited by Krishnan (1948) show 8.26 and 19.10 per cent PbO. Crookshank (1948) describes some of the minerals from the Rajputana pegmatites.

Kasolite, $\text{Pb}(\text{UO}_2)(\text{SiO}_3)(\text{OH})_2(?)$

Kasolite occurs in the silicate zone of alteration as earthy to firm microcrystalline aggregates of minute shreds and fibers. Distinct euhedral crystals such as characterize the Katanga material were not observed. The mineral has a brownish-yellow to pale-brown color, and closely resembles the isostructural species Mineral B (which see). It often occurs more or less admixed with shreds and fibers of uranophane. Kasolite was identified as the principal or sole constituent of the outer silicate zone in uraninite pseudomorphs from Kakanas and Gordonias, Africa; the Ruggles pegmatite, Grafton Center, New Hampshire; and Bisundi, Rajputana, India. It also was observed as a very minor constituent of the silicate zone in material from the Morogoro district, Tanganyika, and a few other localities. At the Ruggles pegmatite, kasolite occurs both as a thin outer crust about the orange gummite pseudomorphs for which the locality is noted and as complete pseudomorphs of a rather porous consistency.

Phosphuranylite, $\text{Ca}(\text{UO}_2)_4(\text{PO}_4)_2(\text{OH})_4 \cdot 7\text{H}_2\text{O}(?)$

Phosphuranylite was observed admixed in small amounts with uranophane in the surface parts of altered uraninite crystals from Spruce Pine,

Mitchell County, North Carolina, and the Ruggles pegmatite, Grafton Center, New Hampshire. Cubical molds of uraninite crystals, some empty and others more or less completely filled with golden-yellow, earthy phosphuranylite were noted in specimens from the Flat Rock mine, Mitchell County, North Carolina; these pseudomorphs, however, appear to be due to the infilling of empty cavities (casts) and not to the alteration of uraninite in place. Phosphuranylite occurs much more commonly as films and coatings on fracture surfaces in the immediate neighborhood of uraninite pseudomorphs in pegmatites (FronDEL, 1950). An occurrence of phosphuranylite(?) with gummite and uraninite in eastern Kuangsi province, China, is described by Nan and Wu (1943).

Rutherfordine, $(\text{UO}_2)(\text{CO}_3)$

Earthy, yellow pseudomorphs of rutherfordine after uraninite crystals were described by Marckwald (1906) from a pegmatite in the Morogoro district, Tanganyika, Africa. Specimens examined from this locality showed a central core of uraninite, a surrounding zone of orange-red gummite, and a pulverulent outer zone of rutherfordine usually much admixed with uranophane and kasolite. The mineral occurs similarly in pegmatite at Newry, Maine, and Beryl Mountain, New Hampshire. A description of the mineral from its known localities is given by FronDEL and Meyrowitz (1956). Rutherfordine effervesces strongly in dilute acids, although the reaction starts slowly, and this provides a useful aid in its recognition. The mineral often is much too fine grained for satisfactory optical study, and an x-ray powder pattern may be required. The uranyl carbonates sharpite and studtite and the carbonates of uranium containing additional cations, such as liebigite, were not encountered in this study. In its known occurrences rutherfordine appears to be produced by the action of carbonated surface waters on the hydrated oxides of the gummite zone.

Schoepite, $2\text{UO}_3 \cdot 5\text{H}_2\text{O}(?)$

Only one example of schoepite was observed in the gummite zone of alteration. It occurs as golden-yellow to yellow, earthy pseudomorphs after uraninite in the Beryl Mountain pegmatite, near Acworth, New Hampshire. Fine-grained Mineral B, uranophane, and rutherfordine were associated. At Katanga, the principal locality for the mineral, schoepite is a drusy or granular massive deposit from solutions and is not a pseudomorphic alteration product. Hacquaert (1927), however, has noted its presence with becquerelite in a uraninite pseudomorph from this locality. Its rarity in gummite is due to the general presence of lead, which leads to the formation of hydrated oxides such as vanden-

driesscheite and fourmarierite. Schoepite also was observed as a yellow crust on massive uraninite from Hottah Lake, Canada, and from the Delta mine, San Rafael Swell, Utah.

Sklodowskite, $\text{Mg}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$

Sklodowskite was not identified in the present study among the uranium silicates comprising the outer zone of alteration. It has been observed, however, by Hacquaert (1927) with curite and cerussite comprising pseudomorphs after uraninite from Kasolo, Katanga.

Soddyite, $(\text{UO}_2)_5(\text{SiO}_4)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$

Soddyite was identified only once in the present study, although its presence in very small amounts admixed with uranophane was suspected in material from a number of localities. It occurs abundantly at the Ruggles pegmatite, Grafton Center, New Hampshire, as complete pseudomorphs after uraninite. These are yellow to straw-yellow in color, with a dense to almost pulverulent consistency, and are composed of minute shreds and fibers of soddyite admixed with small amounts of uranophane. In the hand specimen they resembled very closely the earthy types of uranophane and Mineral *B* pseudomorphs from this and other localities. Soddyite also has been found in the Norrabees pegmatite in Namaqualand, South Africa (Gevers, Patridge, and Joubert, 1937), where it presumably is an alteration product of uraninite. Soddyite may be present in a gummite pseudomorph from Alto do Tibiri, Paraiba, Brazil, analyzed by Florencio (1951) (column 14, Table 1). Microcrystalline soddyite is rather similar optically to beta-uranophane and phosphuranylite, although it lacks the distinct golden pleochroism of the latter, and is best identified by *x*-ray methods.

Uranophane, $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$

The occurrence of a calcium uranyl silicate in the outermost, greenish zone of alteration of uraninite pseudomorphs, bordering on and veining the orange-red gummite zone, was established chemically by Genth (1879) and Von Foulton (1883) in material from pegmatites in Mitchell County, North Carolina. A probably identical mineral occurring as an alteration of uraninite from Arendal, Norway, was analyzed by Norden-skiöld (1884). The existence of uranophane in the siliceous outer zone in such pseudomorphs also was noted by Hidden (1881), Tipper (1919), Hacquaert (1927), Ross, Henderson and Posnjak (1931), Ellsworth and Osborne (1934), Buttgenbach (1922), Schoep (1921), Sarkar and Sen (1946), and others. The first specimen sent to Belgium after the discovery of uranium in Katanga in 1913 was described by Buttgenbach (1926) as

pitchblende altered to gummite and uranophane. This mineral has been called uranophane (or uranotil) in the older literature, but it was shown by Nováček (1935) and Steinocher and Nováček (1939) that the compound is dimorphous, orthorhombic (uranophane) and monoclinic (beta-uranophane). The distinction between these polymorphs rests chiefly on optical and x-ray criteria.

There is also the question of the identity of uranophane and uranotil. Both names are found in some modern literature, as distinct species, based on the belief that the acicular calcium uranyl silicate from Wölsendorf, Bavaria, described by Bořický (1870) under the name uranotil differs in composition from the very similar mineral described earlier from Kupferberg, Silesia, by Websky (1853) as uranophane. Websky's analysis unfortunately was made on very impure material. An x-ray and optical study made here of uranophane from Kupferberg and of uranotil from Wölsendorf has shown conclusively that these two minerals are identical. The name uranophane (and beta-uranophane) should be employed for the species, as was already concluded by Dana (1892).

The uranophane of the silicate zone of alteration generally appears as a hard, dense mass, without structure visible to the unaided eye, and has a waxy to subvitreous luster. The color of the mineral commonly is a pale greenish yellow, but varies to yellowish green, dull green, yellow, orange yellow, and straw yellow. Occasionally it forms relatively soft to porous masses with a dull to earthy luster and a straw-yellow to brownish-yellow color. Under the microscope, the mineral is microcrystalline and composed of shreds or fibers in a confused or matted array. There is almost always at least a small degree of admixture with other minerals. The indices of refraction may be difficult to obtain accurately, because of small particle size. Beta-uranophane, which otherwise resembles the present species very closely, has higher indices and the extinction is inclined (Table 3). The x-ray patterns of the two minerals are quite different (Table 4). Uranophane (and beta-uranophane) ordinarily are separated from the central core of uraninite pseudomorphs by an intermediate zone of gummite, from which the silicates have been derived. In a few instances, however, uranophane was observed forming directly from uraninite.

Uranophane was identified as the chief constituent of the silicate zone in specimens from a large number of localities. These included numerous places in the pegmatite districts of North Carolina, New Hampshire, Maine, Connecticut, Colorado, and the Black Hills, South Dakota. Among the foreign localities may be mentioned Calamuchita, Córdoba, Argentina; Rajputana, India; Karelia, Russia; Katanga, Belgian Congo; Morogoro, Tanganyika. The mineral also was identified as fibrous crusts

and aggregates associated with altering uraninite, but not pseudomorphous after it, from Lake Athabaska, Saskatchewan, and Theano Point, Lake Superior, Canada; Joachimsthal, Bohemia; Katanga district, Belgian Congo; Wölsendorf, Bavaria; the Grants area, New Mexico; the Marysvale and Henry Mountains districts, Utah.

A specimen from Mitchell County, North Carolina, showed a uraninite cube that had been wholly altered to a soft, porous, straw-yellow aggregate of uranophane. A chemical analysis of this material by F. A. Gonyer, cited below, is of interest in showing the presence of a considerable amount of thorium and yttrium in substitution for calcium. A semi-

CaO	ThO ₂ and Y ₂ O ₃	UO ₃	SiO ₂	H ₂ O	Total
5.77	2.60	66.40	13.40	11.71	99.88

quantitative spectrographic analysis by H. C. Harrison showed that Y composed about 10 per cent of the mixed (Th, Y) oxides. Optically, this material had $\alpha \sim 1.642$ (nearly colorless), $\gamma \sim 1.668$ (pale yellow) in Na light, with Z parallel to the elongation.

Vandendriesscheite, $\text{PbO} \cdot 7\text{UO}_3 \cdot 12\text{H}_2\text{O} (?)$

The problems attending the identification of vandendriesscheite have been discussed earlier under fourmarierite, which see. Vandendriesscheite was identified in gummite pseudomorphs from the following localities: numerous places in the Spruce Pine district, Mitchell County, North Carolina, including the Wiseman, McKinney, Deak and various unstated mines in this district; Newry, Maine; the Palermo and Ruggles pegmatites in New Hampshire; numerous specimens from the Katanga district, Belgian Congo; Joachimsthal, Bohemia. The mineral also occurs as crusts and minute crystals (the "Mineral X" of Palache and Berman, 1933) on altering uraninite at Great Bear Lake, Canada. It was observed as their colloform films on uraninite from Hottah Lake, N.W.T., Canada. Vandendriesscheite was doubtfully identified from a number of other localities, and the mineral appears to be more common than fourmarierite. It often occurs admixed with other oxidic minerals of both higher and lower indices, and uranophane is commonly present in small amounts. Vandendriesscheite occurs as dense microcrystalline aggregates. The color varies from yellow-orange, brownish orange, and orange to orange-red. The reddish shades are less typical than with fourmarierite. Usually only the mean index of refraction can be measured due to small particle size; this varies from about 1.77 to 1.82. Some material doubtfully identified as vandendriesscheite had α as low as about 1.71–1.74. There seems to be little doubt that the indices of refraction of this min-

eral vary over at least 0.04 due to compositional variation, presumably a substitution of Ba or Ca for Pb.

Unidentified Mineral A

This mineral was recognized in the gummite zone of specimens from six localities: pegmatites at North Wilton, Palermo, Ruggles, Alstead, and Beryl Mountain, all in New Hampshire, and a pegmatite at Grassy Creek, Mitchell County, North Carolina. The latter specimen was one of those described and analyzed by Von Fouchon (1883) in his study of gummite. Mineral *A* is particularly abundant at the Ruggles locality, where it is one of the chief constituents of the orange gummite pseudomorphs after dendritic aggregates of uraninite crystals for which the locality is noted (see Shaub (1938)). The mineral was recognized as a distinct and presumably new species on the basis of its x-ray powder pattern (Table 4). It occurs as microcrystalline aggregates of a bright-orange to orange-yellow or golden-yellow color. The reddish shades of color seen in many fourmarierite and some vandendriesscheite specimens are lacking. The luster varies from dull and earthy to weakly vitreous in hard, translucent aggregates. Under the microscope the mineral is yellow in color, not perceptibly pleochroic, and has low to moderate birefringence. Only the mean index of refraction could be obtained. This varies between 1.78 and 1.88 in most specimens, but one specimen from the Ruggles pegmatite had $n \sim 1.96$. Semiquantitative spectrographic analyses show that the mineral is an oxide of uranium or a uranate containing Pb, K, Na, Ca, and Ba in significant amounts. The Ruggles material with $n \sim 1.96$ contained Pb between 5 and 10 per cent, K and Ca 0.5–1 per cent, Na and Ba 0.1–0.5 per cent. Material from Palermo with $n \sim 1.84$ contained both Pb and K in the range 1 to 5 per cent, and Ca, Ba and Na in the range 0.1 to 0.5 per cent. Possibly several different isostructural minerals varying in the mutual substitution of Pb, K, Ca, etc., with accompanying variation in the indices of refraction, are represented. The x-ray patterns of all specimens are virtually identical. There was a complete change in the x-ray pattern of the Ruggles material after heating to 500° C. Study of this mineral is continuing.

Unidentified Mineral B

Mineral *B*, apparently the calcium analogue of kasolite, is a relatively common constituent of the silicate zone of alteration. It was first recognized as a probable new species during the present study, and a detailed description is in the course of preparation. Mineral *B* occurs as dense to earthy microcrystalline aggregates composed of minute shreds and fibers. Its color is straw yellow to pale yellowish brown, and lighter than

typical kasolite. The x-ray powder pattern is virtually identical with that of kasolite, but the indices of refraction are considerably less (Table 3). The presence of calcium as a major constituent was established by chemical tests. The mineral often is so fine grained that only the mean index of refraction can be obtained; this usually ranges between 1.81 and 1.84. Admixture with uranophane is common. Mineral *B* occurs both as complete pseudomorphs and as zones surrounding orange-red gummite; it also has been observed as earthy crusts along fracture surfaces in the matrix. The mineral was recognized from the following localities: the Bob Ingersoll pegmatite, Pennington County, South Dakota; the Ruggles pegmatite near Grafton Center, and the Beryl Mountain pegmatite near Acworth, both in New Hampshire; the Mica Lake area, Hahn's Peak, Colorado; and Bisundi, Rajputana, India. It was doubtfully identified in material from Karelia, Russia, and several other localities.

Unidentified Mineral C

This apparently new species was recognized on the basis of its x-ray powder pattern (Table 4). The pattern closely resembles but is distinct from the patterns of fourmarierite and schoepite. The pattern seems to be definite and characteristic as it was given by natural material from five different localities and also by a sample of synthetic hydrated lead diuranate. Mineral *C* occurs in the gummite zone of alteration as dense, microcrystalline aggregates with an orange-brown, reddish-brown or chocolate-brown color. The powder is mustard yellow. The color differs from the orange-red color of fourmarierite and some vandendriesscheite, and the yellow to orange color of Mineral *A*. Clarkeite, however, has a very similar color. The mineral was observed from the following localities: Mitchell County, North Carolina, at the Wiseman mine (analysis 4, Table 1), the McKinney mine, and at an unstated locality (analysis 12, Table 1); Easton, Pennsylvania, where it is an alteration of uraninite or uranoan thorianite; Newry, Maine. The material from the Wiseman mine is that described by Ross, Henderson and Posnjak (1931). The optics given by these authors for "gummite" do not refer to the present mineral; the material of their analysis sample, here examined, has indices between 1.77 and 1.82. A similar range is shown by the material from the other localities stated, with the exception of the material of analysis 12, Table 1, from Mitchell County, which has higher indices, 1.85–1.89. The indices are considerably lower than those of fourmarierite and clarkeite, but comparable to those of vandendriesscheite. Schoepite has much lower indices of refraction. The fine-grained nature of the material makes optical study difficult. The two available analyses of this mineral, cited in Table 1, were made on slightly inhomogeneous material.

A semiquantitative spectrographic analysis of the Easton material showed U as the major constituent with Th, Pb, Ca, and Ba present in amounts between 1 and 10 per cent. Mineral C apparently is related structurally to fourmarierite. A further description of this mineral with additional analyses is planned.

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TABLE 3. OPTICAL PROPERTIES OF MINERALS PRESENT IN GUMMITE

Name	Symmetry	Indices and pleochroism			Sign, 2V, Disp.	Remarks
		α	β	γ		
Becquerelite	Orthorhombic	1.72-1.75 pale yellow	1.81-1.82 deep yellow	1.82-1.83 deep yellow	(-), 30° $r > v$	X perp. cleavage.
Beta-uranophane	Monoclinic	1.66-1.67 colorless	1.68-1.69 lemon-yellow	1.69-1.71 lemon-yellow	(-), 40°-70°, $r > v$	X = b , Z / \angle elong. = 18°-57°. Fibers.
Clarkeite	Orthorhombic?	2.00 Color brown-yellow	2.10 brown	2.11 to reddish	(-), mod. $r < v$	Indices vary; some with mean index 1.94-1.97
Curite	Orthorhombic	2.05-2.06 pale yellow	2.07-2.11 light red-orange	2.11-2.15 dark red-orange	(-), large $r > v$	Z = elong.
Fourmarierite	Orthorhombic	1.85-1.86 colorless	1.90-1.92 pale yellow to orange	1.90-1.94 yellow to orange	(-), mod. to large $r > v$	X perp. cleav., Y = elong.
Kasolite	Monoclinic	1.88-1.90 Nearly colorless	1.90-1.91	1.94-1.96 pale yellow	(+), 42°	X = elong. Faint yellow pleochroism. Fibers.
Masuyite	Orthorhombic	1.785 pale yellow	1.906 deep golden	1.917 deep golden	(-), 50°, $r > v$	X perp. cleav. Also with indices 2.11-2.15 (?).
Meta-autunite	Tetragonal	1.58-1.60 pale yellow	1.59-1.61 yellow	1.59-1.61 yellow	(-), 0° to small, $r > v$	X perp. plates and cleavage. Indices and 2V vary with H ₂ O.
Mineral A	Not known	Mean index 1.78-1.88, variable			(+) mod.	Yellow. Not pleochroic (?). Also with $n = 1.96$.
Mineral B	Monoclinic	1.825 Nearly colorless	~1.84 to pale yellow	1.867	(+) mod.	Mean index 1.81- 1.83 when fine grained. Faint pleochroism.
Mineral C	Not known	Mean index 1.77-1.82, variable, in part higher?			(+) mod.	Orange-brown. Not pleochroic ?
Phosphuranylite	Orthorhombic	1.66-1.67 pale yellow	1.70-1.72 golden yellow	1.70-1.72 golden yellow	(-), 5°-25°, $r > v$	Z perp. plates. Indices increase with Pb content.
Rutherfordine	Orthorhombic	1.721 pale yellow	1.729 golden yellow	1.757 greenish yellow	(+), large	Y = elong.
Schoepite	Orthorhombic	1.69-1.70 colorless	1.71-1.72 lemon-yellow	1.73-1.74 lemon-yellow	(-), large $r > v$	X perp. cleavage.
Skłodowskite	Orthorhombic	1.613	1.635 color pale yellow	1.657	(-), large	Y = elong.
Soddyite	Orthorhombic	1.65 colorless	1.68 pale yellow	1.71 pale green-yellow	(-), large $r > v$	Often cloudy.
Uranophane	Orthorhombic	1.64 colorless	1.66 golden yellow	1.67 golden yellow	(-), small $r > v$	Z = elong. Parallel.
Vandendriesscheite	Orthorhombic	1.76-1.79 colorless	1.81-1.84 golden yellow	1.82-1.85 golden yellow	(-), med. $r > v$	X perp. cleavage. Mean index 1.77- 1.82.

TABLE 4. X-RAY POWDER DATA FOR MINERALS IN GUMMITE

Copper radiation, nickel filter, in Ångströms

Note: In most instances only the inner lines of the patterns are cited, sufficient to ensure discrimination.

Becquerelite		Beta-uranophane		Clarkeite		Curite	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
1	8.51	10	7.83	1	10.98	10	6.28
10	7.50	4	6.66	1	8.33	1	4.80
2	6.63	4	6.10	2	6.70	4	4.55
1	6.24	4	5.07	8	5.77	1	4.17
1	5.63	4	4.85	4	4.09	9	3.97
6	4.71	4	4.55	9	3.34	4	3.53
1	4.31	3	4.11	10	3.17	4	3.36
8	3.75	9	3.90	3	2.92	8	3.14
8	3.56	1	3.75	5	2.69	4	3.07
2	3.48	6	3.51	4	2.61	2	2.93
2	3.39	1	3.41	3	2.45	1	2.81
9	3.22	2	3.35	2	2.06	4	2.70
1	3.13	5	3.19	7	1.968		
2	2.97	4	3.04	6	1.863		
		3	2.99				
		2	2.91				
		4	2.83				
		3	2.78				
		5	2.59				

Fourmarierite		Kasolite		Phosphuranylite		Rutherfordine	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
2	7.86	6	6.61	1	10.16	10	4.60
4	6.83	2	6.19	10	7.83	8	4.27
9	3.45	4	5.31	1/2	7.20	8	3.87
10	3.09	2	4.76	1	6.33	9	3.20
4	2.73	8b	4.19	8	5.83	5	2.62
6	2.44	7	3.53	1/2	5.37	2	2.48
5	2.26	1	3.38	1	4.96	3	2.41
2	2.15	10	3.26	2	4.72	4	2.28
2	2.09	5	3.07	3	4.33	6	2.14
6	1.996	9	2.93	9	3.97	8	2.04
8	1.907	3	2.73	1	3.83	1	1.94
2	1.817	3	2.64	1	3.44	3	1.91
				2	3.36	2	1.87
				6	3.12	2	1.73
				4	3.07		
				2	2.94		
				6	2.86		

b=broad line.

TABLE 4. X-RAY POWDER DATA FOR MINERALS IN GUMMITE—*Continued*

Schoepite		Sklodowskite		Soddyite		Uranophane	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
10	7.49	10	8.42	8	6.14	10	7.88
1	6.74	2	6.37	3	4.71	4	6.61
2	6.09	5	5.91	9	4.48	4	5.42
2	4.08	4	4.82	2	3.73	5	4.76
8	3.64	1	4.51	10	3.32	2	4.29
9	3.26	4	4.33	2	3.22	9	3.94
1	3.01	8	4.19	3	2.95	4	3.60
2	2.83	5	4.00	2	2.78	4	3.51
7	2.60	6	3.52	7	2.69	1	3.41
3	2.48	7	3.27	6	2.47	1	3.35
2	2.35	6	3.00	1	2.39	5	3.20
1	2.27	5	2.87	2	2.32	1	3.09
1	2.21	2	2.80	2	2.26	8	2.99
4	2.10	2	2.74	1	2.18	8	2.91
6	2.05	1	2.70	4	2.09		
1	1.981	1	2.66				

Vandendriesscheite		Mineral A		Mineral C	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
2	8.27	7	6.37	5	6.95
10	7.31	10	3.49	1	5.85
3	6.49	7b	3.18	1	4.12
1	4.85	5	3.02	10	3.46
2	4.39	3b	2.61	10	3.09
1	4.14	1	2.09	1	2.77
2	3.93	2	2.00	3	2.44
8	3.58	3b	1.92	2	2.29
1	3.37	1	1.81	5	1.991
9	3.19	3	1.75	6	1.916
1	3.00	1	1.57	6	1.730
3	2.73	1	1.52	4	1.673
5	2.53			2	1.548
2	2.40			1	1.509
1	2.32			2	1.383
2	2.05			1	1.355
7	1.989			2	1.305
3	1.908			2	1.283

b=broad line.

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PRECISION DETERMINATION OF LATTICE CONSTANTS OF SINGLE CRYSTALS USING THE CONVENTIONAL WEISSENBERG CAMERA*

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ABSTRACT

A rapid, routine method is described for determining lattice constants of medium precision from single crystals with the conventional Weissenberg camera. The method involves the determination of a film correction factor, as a function of the reflection angle θ , from the powder pattern of a standard calibration substance exposed on the zero-level Weissenberg film of the single crystal. Lattice constants are obtained by the Bradley and Jay graphical extrapolation method. The experimental results on quartz and colemantite indicate that a precision of about 2 to 4 parts in 10,000 may be easily attained, and that the method is probably inherently capable of giving more precise results.

INTRODUCTION

Lattice constants of high precision may be determined readily by x-ray powder diffraction methods for crystalline materials having at least tetragonal or hexagonal symmetry (see e.g. Buerger, 1942, Chap. 20; Klug and Alexander, 1954, Chap. 8; Peiser, Rooksby, and Wilson, 1955, Chap. 15). The techniques employed depend upon the existence of sharp, sufficiently intense, and unequivocally indexable lines in the region of θ near 90° . For crystals of symmetry lower than tetragonal or hexagonal these conditions do not obtain and recourse must be made to single-crystal methods.

The theory governing the determination of precise lattice constants from single crystals is the same as that used in the powder methods (see refs. above). Briefly, the strategy usually employed is to obtain accurate high θ -values, relatively free from film shrinkage and camera radius errors, and to eliminate other errors, mainly those caused by specimen absorption and camera eccentricity, by graphical or analytical extrapolation methods. Buerger (1937) has suggested the use of a Weissenberg "back-reflection" camera to minimize film shrinkage and camera radius errors. Farquhar and Lipson (1946) have published a similar back-reflection technique employing the oscillating crystal principle. Weisz, Cochran, and Cole (1948) have described a method using the conventional Weissenberg camera in which the θ -values are obtained accurately by measuring on the rotation axis circle of the instrument the angular settings of the crystal giving peak intensities.

The first two of these methods require special cameras, not available commercially, and in addition the method of Farquhar and Lipson is

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difficult to apply to the monoclinic and triclinic cases.^{*} The method of Weisz et al. which makes use of the conventional Weissenberg camera and is readily applied to the monoclinic and triclinic cases, is however, according to the authors, lengthy and tedious when photographic techniques are used to fix peak intensities.

The present investigation was aimed at developing a method which would yield lattice constants of moderate precision in a rapid and routine way, using only readily available equipment. It was found possible to do this in the way described below.

DESCRIPTION OF THE METHOD

Preparation and calibration of film

A zero-level Weissenberg pattern of the crystal under investigation is made in the usual way except that the translation motion stop of the instrument is set so that a clear space about 2 cm. in width at one edge of the film is maintained. The goniometer head carrying the crystal is then replaced by a head bearing a powder spindle of a substance used as a calibrating agent. The Weissenberg layer screen is replaced by a screen having a slit 1 cm. in width, and the powder pattern of the calibrating substance recorded on the clear space of the film. A typical composite Weissenberg and powder pattern is shown in Fig. 1. The powder pattern screen used was made up simply by adding a removable slotted brass cylinder to the rotation shield furnished with the Weissenberg camera, as illustrated in Fig. 2. It was found that the use of the regular Weissenberg screen for the powder pattern recording was not satisfactory because of the narrow width (0.25 cm.) of the resulting powder pattern which precludes its accurate measurement.

After photographic processing the washed film is allowed to air-dry in a draft-free room, reasonable care being exercised to keep the film free of strain during drying. After at least two weeks aging the film is measured. Measurements of the spots and lines are made (at one sitting) to the nearest 0.01 cm. using a measuring device somewhat similar to that shown by Buerger (1942, p. 446). A 4× hand lens is used as an aid in setting the hair-line.

A calibration curve for a given film is then prepared by plotting the ratio $k(\theta) = (\theta_{\text{theoretical}})/(\theta_{\text{measured}})$ vs. θ_{measured} for the calibrating substance. A typical calibration curve is shown in Fig. 3. The film constant $k(\theta)$ is then multiplied into the measured θ -values for the crystal to give corrected θ -values, from which d -spacings are calculated. This method of correction essentially eliminates errors due to film shrinkage (linear or nonlinear), as well as any continuous departure from radial symmetry in the camera. This will be true, of course, only if the measurements made on

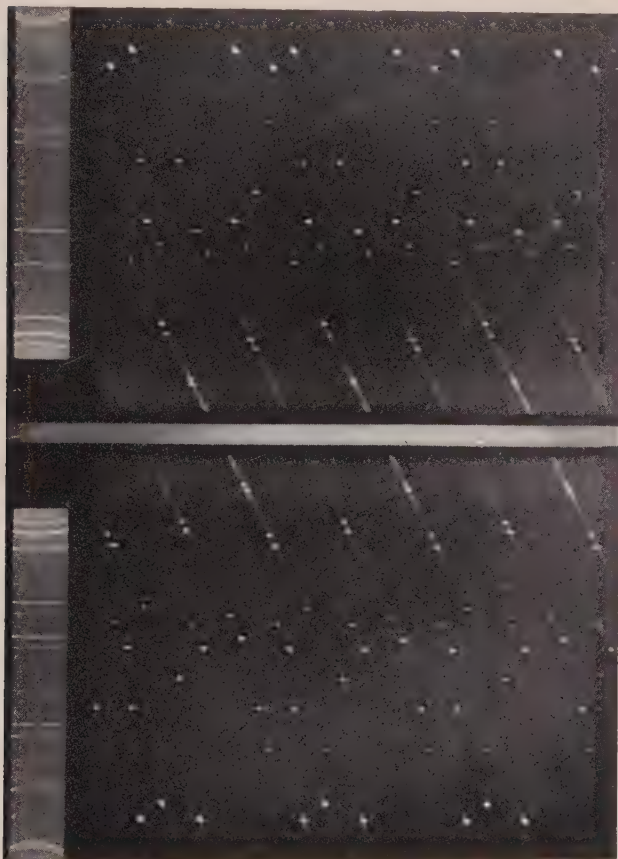


FIG. 1. Composite Weissenberg pattern of quartz around [001] and calibration powder pattern of silver.

the calibrating powder pattern at the edge of the film hold along the rest of the film. This question was examined by measuring powder patterns exposed at various places along the width of the film, and it was found that within a sufficient degree of approximation the calibration made at one edge of the film did hold for the rest of the film. Nevertheless, whenever possible the spots measured on the Weissenberg part of the film were taken close to the calibration pattern.

Calibration standards

Both quartz and silver were used as calibrating standards. The quartz was from a crystal fragment of clear material from Hot Springs, Arkansas, used in a powder spindle about 0.18 mm. in diameter. The silver was

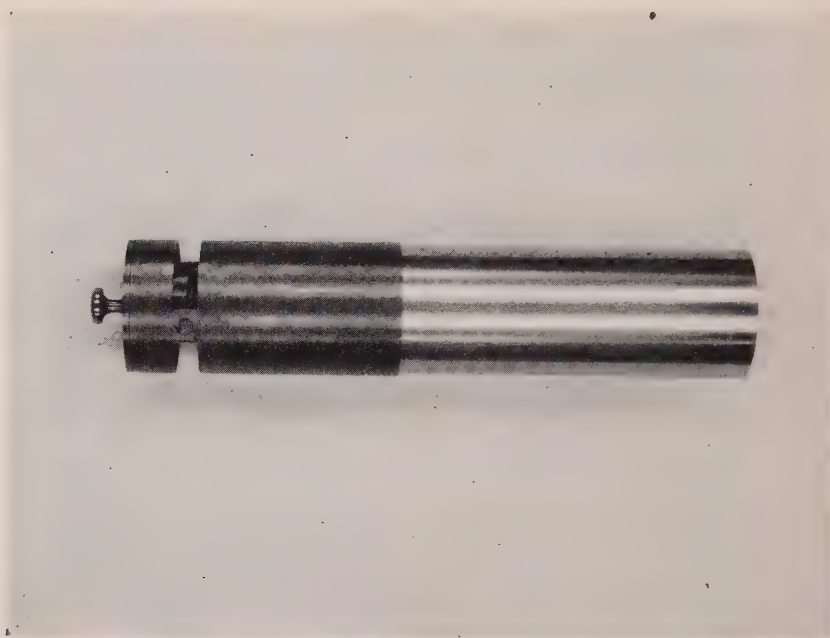


FIG. 2. Photograph showing rotation shield with removable slotted brass cylinder for recording powder pattern.

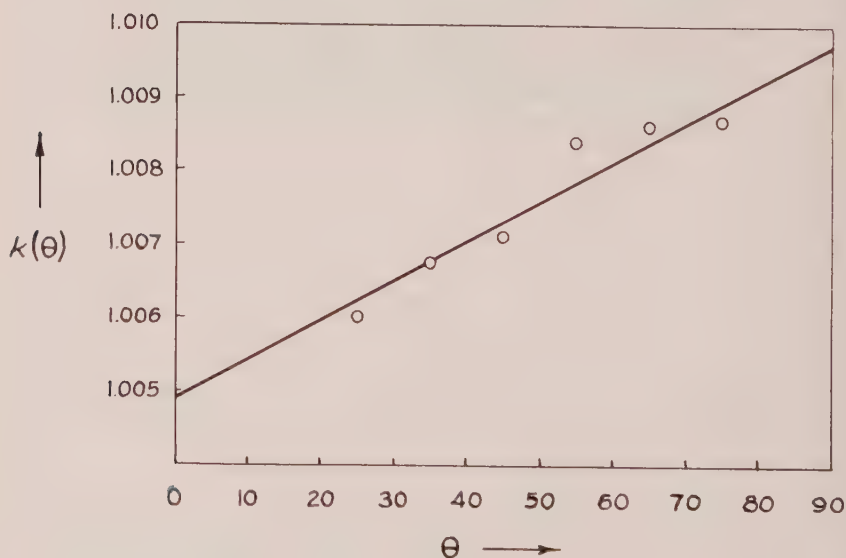


FIG. 3. Typical plot of $k(\theta)$ vs θ for calibration of Weissenberg pattern. $k(\theta)$ values averaged for 10° intervals and plotted at midpoint of interval.

Eimer and Amend, C. P. "precipitated powder," annealed in air at about 350 °C. for approximately 18 hours. The silver as taken from the bottle does not give sharp lines. The silver powder spindle used was 0.07 mm. in diameter. A spectrographic analysis of the silver, made by Richard S. Harner (then of the U. S. Geological Survey), yielded the following results:

0.0X% Cu, Si, Mg with estimated Cu < 0.05%
0.00X Al, Fe, Ca
0.000X Ni, Be, Cr

Thus, the silver is of sufficiently high purity so that the accurately measured lattice constant (Table 1), given in Straumanis and Ievins (1940, p. 100) may be assumed to apply.

With experience, it became apparent that silver was superior to quartz as a calibrating agent for the task at hand, mostly because its pattern is simpler and the lines in the back-reflection region are stronger and sharper. Obviously there are other standards that could be used. A discussion of the criteria that standards should meet, together with a list of standards and tables of their reflection angles (including those for quartz), has been given by Parrish (1953). The precise reflection angles for silver, however, have not appeared in the literature. These are given in Table 1.

The lattice constants of quartz were taken as follows: $a = 4.9131 \text{ \AA}$ and $c = 5.4046 \text{ \AA}$ (18° C.). These values in Angstrom units were obtained from those given in kX units by Wilson and Lipson (1941), by multiplying the kX values by 1.00202. The values of the lattice constant of silver and the wave lengths used to calculate reflection angles for it are given in Table 1.

Calculation of the single-crystal lattice constants

From the d -spacings, obtained from the corrected θ -values as explained above, the apparent values of the lattice constant of interest are calculated, these plotted against $\sin^2\theta$, and the linearly extrapolated value at $\sin^2\theta = 1$ taken as the true lattice constant, following the method of Bradley and Jay (1932).

Various other extrapolation functions have been proposed for use in the graphical extrapolation method (Nelson and Riley, 1945). The possibility of the use of other appropriate functions was considered briefly during this work, but these were not investigated systematically, mainly due to the fact that the use of the $\sin^2\theta$ plot gave such excellent results.

The values of the wavelengths used in calculating d -spacings of the single crystals studied were taken from Bragg (1947), and are:

CuK: $\lambda\beta_1 = 1.39217 \text{ \AA}$ $\lambda\alpha_1 = 1.54050$ $\lambda\alpha_2 = 1.54434$ $\lambda\alpha = 1.5418$

RESULTS

Measurements on quartz

As a check of the method the lattice constant a of a single, clear, natural crystal of quartz (locality unknown) was measured using the hkl reflections, and using silver as the calibration standard. The value $a = 4.9130 \pm 0.0005 \text{ \AA}$ (approx. 23° C.) was obtained, in good agreement with the values 4.9131 \AA (18° C.) of Wilson and Lipson (1941) and 4.9125 \AA (18° C.) of Keith (1955). These latter values were obtained by

TABLE 1. PRECISE REFLECTION ANGLES FOR SILVER*

Ag, face-centered cubic, $a = 4.07784 \text{ kX}$ (25° C.)			
CuK: $\lambda\beta_1 = 1.38935 \text{ kX}$			
$\lambda\alpha_1 = 1.537395$			
$\lambda\alpha_2 = 1.541232$			
$\lambda\alpha = 1.53867$			
$\lambda\alpha = (2\lambda\alpha_1 + \lambda\alpha_2)/3$			
hkl	θ°	hkl	θ°
111	17.161 β	400	42.965 β_1
	19.057 α_1		48.941 α_1
	19.100 α_2		49.106 α_2
	19.073 α		48.996 α
200	19.920 β	331	47.950 β_1
	22.149 α_1		55.254 α_1
	22.207 α_2		55.461 α_2
	22.168 α		55.323 α
220	28.806 β	420	49.628 β_1
	32.221 α_1		57.462 α_1
	32.311 α_2		57.687 α_2
	32.251 α		57.537 α
311	34.403 β	422	56.572 β_1
	38.698 α_1		67.443 α_1
	38.813 α_2		67.790 α_2
	38.736 α		67.558 α
222	36.166 β	511, 333	62.275 β_1
	40.769 α_1		78.381 α_1
	40.893 α_2		79.099 α_2
	40.810 α		
		440	74.509 β_1

* Lattice constant of silver and wave-length values from Straumanis and Ievins (1940, p. 100).

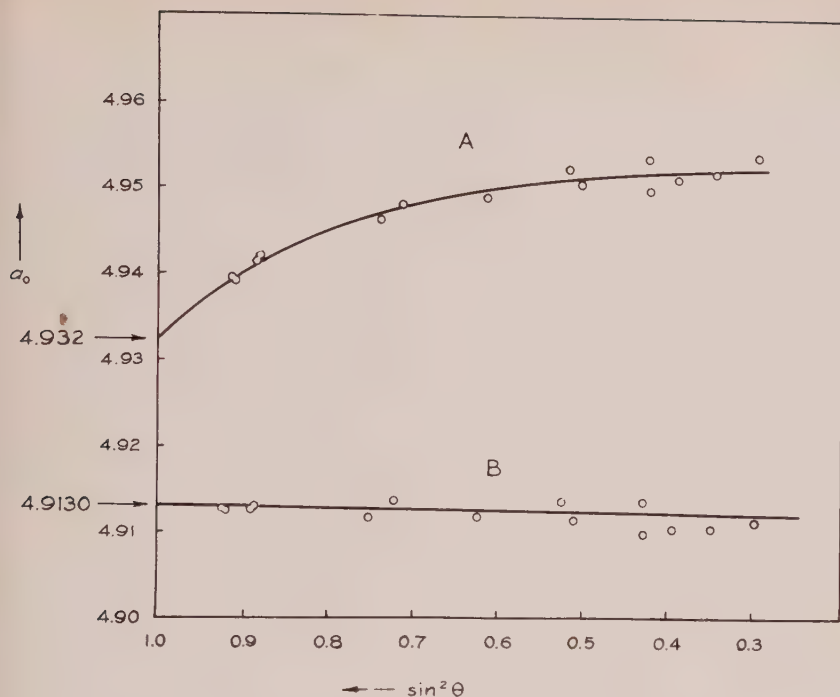


FIG. 4. Determination of a for quartz.

Curve A plot of apparent values of a derived from *uncorrected* θ -values. $a = 4.932 \pm 0.001$ Å.

Curve B plot of apparent values of a derived from *corrected* θ -values. $a = 4.9130 \pm 0.0005$ Å.

Calibrating standard, silver.

the more precise powder method and as quoted have been rounded-off to five significant figures.

The results obtained for quartz are shown plotted in two ways in Fig. 4. It is seen from this that when the apparent lattice constants derived from uncorrected θ -values are used the extrapolation is not linear, but has in fact the form predicted from the analysis of the error function (Buerger, 1942, p. 419).

A comparison of the values for a obtained in several ways from these same data is as follows:

(a) Linear extrapolation using corrected θ -values

$$a = 4.9130 \pm 0.0005 \text{ Å.}$$

(b) Average value of a using four largest corrected θ -values

$$a = 4.9126 \pm 0.0001 \text{ Å.}$$

(c) Nonlinear extrapolation using uncorrected θ -values

$$a = 4.932 \pm 0.001 \text{ Å.}$$

(d) Average value of a using four largest uncorrected θ -values

$$a = 4.941 \pm 0.001 \text{ Å.}$$

The limits of error quoted are the estimated extrapolation errors for (a) and (c) and the average deviations for (b) and (d).

These results are enlightening. In the first place they show that the practice of calculating an average lattice constant from high θ -values without any correction can lead to quite wrong results, even though the deviation of the individual results from the mean is small. In this case the value of a is off by 0.028 Å, i.e. 0.6%. If the apparent lattice constants derived from smaller θ -values are included in the average the result will be in greater error. It is also seen that, in general, the extrapolation plot using uncorrected θ -values leads to unreliable results. On the other hand, the average obtained from the large corrected θ -values is fairly close to the true lattice constant. The latter result emphasizes the need for at least determining the average effective camera radius for each camera used.

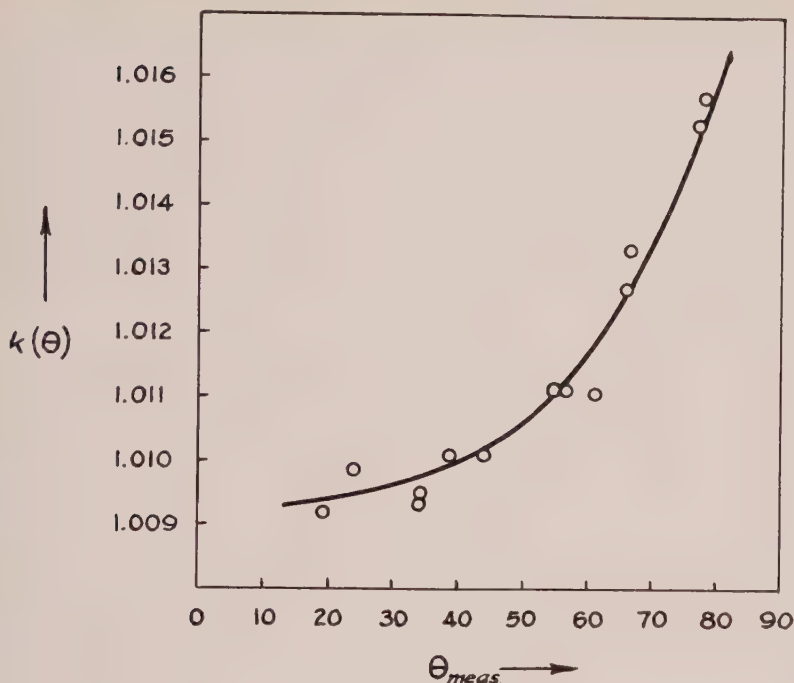
The function $k(\theta)$

It is of interest to inquire as to how $k(\theta)$ varies from film to film for the same camera. In this investigation it was found that $k(\theta)$ is usually a linear function of θ but not always. In fact for the film from which the results for quartz, as cited above, were obtained, the plot of $k(\theta)$ was not linear (Fig. 5). From this it is seen that $k(\theta) = 1.014_5$ at $\theta = 75^\circ$. For the corresponding θ -value in the plot of Fig. 3, $k(\theta) = 1.008_9$. The film from which the $k(\theta)$ plot of Fig. 5 was derived was measured two years after it had been prepared, whereas the other $k(\theta)$ plot was obtained from measurements made two weeks after the film was made, both films having been made in the same camera. It seems likely that the additional correction is due to additional shrinkage over the longer period of time. In both cases the corrections are rather large. Since one would expect a shrinkage correction of not more than about 0.4% for a relatively young film, it follows that the remainder of the correction is due to error in the effective film radius.

Measurements on colemanite

Lattice constant determinations were also made for the monoclinic crystal, colemanite (results previously reported by Christ, 1953). The final values obtained are listed in Table 2. The values of d_{103} , d_{010} , and d_{001} were obtained by graphical extrapolation from measurements of the reflection angles for $h00$, $0k0$, and $00l$, respectively. The plot for d_{010} ($=b$) shown in Fig. 6 is fairly typical of those obtained for d_{100} and d_{001} . Each of these plots had an indicated extrapolation error of ± 0.0005 Å. The value of the angle β was obtained by using the relationship:

$$\cos \beta = \frac{d_{001}d_{100}}{2hl} \left(\frac{h^2}{d_{100}^2} + \frac{l^2}{d_{001}^2} - \frac{1}{d_{h0l}^2} \right).$$

FIG. 5. Plot of $k(\theta)$ used in determination of a for quartz.

The known values of d_{001} and d_{100} and ten values of d_{h0l} from corrected θ measurements in the region of $\theta=75$ to 80° were used to calculate an average β . With this method the probable error for β is $\pm 5'$, leading to the probable errors shown for a and c in Table 2. This method for determining β is relatively inaccurate. Interaxial angles as well as interplanar spacings may be determined precisely by the graphical extra-

TABLE 2. LATTICE CONSTANT MEASUREMENTS FOR COLEMANITE
 $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$, monoclinic, $P2_1/a$

Constant	Present Method	Precession Method
d_{100}	8.2100 ± 0.0005	
d_{010}	11.2637 ± 0.0005	
d_{001}	5.7300 ± 0.0005	
a	8.743 ± 0.004	8.73 ± 0.01
b	11.264 ± 0.002	11.25 ± 0.02
c	6.102 ± 0.003	6.10 ± 0.015
β	$110^\circ 7' \pm 5'$	$110^\circ 10' \pm 5'$

Linear measurements in Ångstrom units. Wavelengths used, CuK: $\lambda\beta_1=1.39217$, $\lambda\alpha_1=1.54050$, $\lambda\alpha_2=1.54434$, $\lambda\alpha=1.5418$ Å.

polation method. However, for the precision sought for the lattice constants of colemanite an error of $\pm 5'$ in β was tolerable and no further work was done on this.

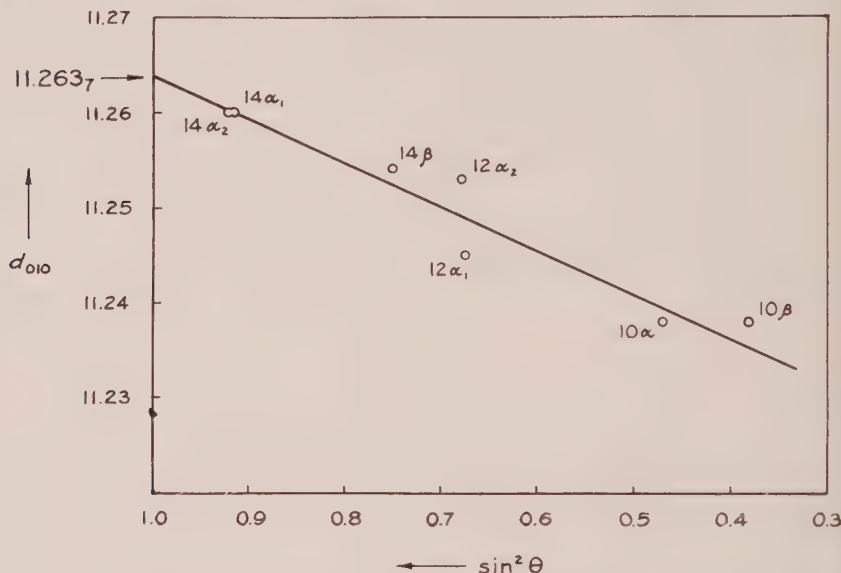


FIG. 6. Determination of d_{010} for colemanite. $d_{010} = 11.2637 \pm 0.0005$ Å. Calibrating standard, silver. Orders of the reflections $0k0$ indicated.

Many more points can be obtained on the plot for a given lattice spacing by using general zone reflections. For example, for the determination of d_{100} , measurements of the angles for the $hk0$ reflections instead of just the $h00$ reflections may be used. The relationships governing the use of general zone reflections and those used in the determination of interaxial angles are given by Weisz et al. (1948).

Some idea of the efficacy of the present method may be gained from the following example. Plots of the values of d_{100} (from $h00$ reflections only) were obtained from two different films which had significantly different $k(\theta)$'s. One film represented the $h0l$ zone and the other the $hk0$ zone. Nevertheless, the two plots gave exactly the same value of d_{100} , namely 8.2100 ± 0.0005 Å. The exact agreement is, of course, fortuitous, but it does indicate that the extrapolation error of ± 0.0005 Å assigned the several Bradley-Jay plots for colemanite is not too small.

The assignment of probable errors to the lattice constants listed in Table 2 was done in the following way. For the interplanar spacings the estimated extrapolation error is listed. The errors for a and c are fixed by

the relatively large error in β . For b the error is taken as four times the extrapolation error as only one determination of b was made. Measurements made on a calibrated, shrinkage-corrected precession film by an independent observer (Joan R. Clark, U. S. Geological Survey) are included in Table 2. These are of lower precision, and the comparison essentially furnishes a check on the precession method. Of particular interest, however, is the precession method measurement of β , as this is a direct measurement independent of the values of d_{100} and d_{001} . It is seen that the two measurements are in excellent agreement.

DISCUSSION

The method described is a rapid and routine method for obtaining lattice constants of moderate precision. It is apparent that in the present study no real attempt has been made to push the method to its utmost limits of precision. The Weissenberg camera used is a typical commercial instrument. The measuring device employed gives readings directly with vernier only to the nearest 0.01 cm., with the possibility of estimating whether the third figure is nearer to 0.000 or 0.005 cm. Similarly, unless a gross error was detected, readings of line or spot positions were usually made only once. The crystals used were of moderate size; for example, the quartz crystal measured had a projected width on the film of 0.3 mm. at $\theta = 70^\circ$. Obviously, for higher accuracy a more precise measuring device could be used, averages of several θ measurements used instead of a single one, and crystals of smaller size employed.

Despite the relatively unrefined techniques used the results obtained are good. It would be necessary to carry the investigation further to establish accurately the limits of precision, but from what has been done it seems likely that the method will yield lattice spacings precise to 2 to 4 parts in 10,000. The precision of the corresponding unit-cell constants depends upon the precision with which intervector angles can be determined in the monoclinic or triclinic cases. As was pointed out above, these angles can be determined with the same degree of precision as the lattice spacings using the relationships listed by Weisz et al. (1948). In the Bradley-Jay plots obtained by the present method the extrapolation is linear to fairly low values of $\sin^2\theta$. In view of the approximations inherent in the Bradley-Jay method these results are somewhat surprising, albeit very welcome.

It is perhaps not out of place here to point out that in many papers in the mineralogical literature lattice constants determined from rotation or Weissenberg patterns are given with an implied precision of 1 part in a 1000 or better. It is clear from the context of the same papers that, barring fortunate accidents, these results have a probable error of from 0.5

to 1.0%. It is suggested that when results of precision better than 0.5% are desired, at least an average film constant for the camera in use be obtained.

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MANGANPYROSMALITE, BUSTAMITE, AND FERROAN JOHANNSENITE FROM BROKEN HILL, NEW SOUTH WALES, AUSTRALIA

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SUMMARY

Manganpyrosmalite has been found in material from Broken Hill, New South Wales, where it occurs in association with ferroan johannsenite and calcium-poor bustamite. A partial analysis of manganpyrosmalite and a complete one for johannsenite have been made, and full optical properties for the three minerals are reported. X-ray powder data are recorded in addition to a Weissenberg study of the manganpyrosmalite. Transformation of the clinopyroxene into a manganese-iron wollastonite solid solution has been effected in the laboratory and the x-ray data for these materials are given.

INTRODUCTION

Before their discovery of a manganese analog of pyrosmalite at Sterling Hill, New Jersey, pyrosmalite had been described, according to Frondel and Bauer (1953, p. 755) from only two localities, *viz.* the magnetite deposits of Nordmark and Dannemora in Sweden. The writer has now recognized manganpyrosmalite in material from Broken Hill, New South Wales, and in view of its apparent rarity it would seem desirable to record the data determined for this mineral from this locality.

Before proceeding to its description it should be pointed out that the writer has been unable to find any record of the occurrence of pyrosmalite at Broken Hill in the literature available to him, other than its mere inclusion in a listing of mineral species reported from the main Broken Hill Lode, and the Pinnacles Mine, some 8–10 miles south-west from Broken Hill itself (Woodward, 1952, p. 63). Specific data as to physical properties, exact location, and occurrences were not given.¹

The specimen on which manganpyrosmalite was found was collected by Mr. Roy ("Floss") Campbell of Broken Hill in the South End of the 12th level of the Zinc Corporation workings, and it was given to the present author during a period spent collecting material with the kind permission and assistance of the Geological Staff of the Zinc Corporation.

¹ After this paper was written Dr. Austin Edwards very kindly gave the present writer the following information: "(1) Pyrosmalite, both manganese-rich and manganese-poor, was discovered in the Broken Hill lode by M. A. Mawby (now the President of Consolidated Zinc Pty. Ltd.) about fifteen years ago. He had both varieties analysed, and the identification confirmed by x-ray patterns, but the discovery was not published. (2) Dr. Stillwell rediscovered these two minerals independently about two years ago, in the course of the major investigation of the mineral composition of the Broken Hill lode. He separated them, and had them analysed, and I think, x-rayed."

It is a very great pleasure to be able to record one's thanks to the staff of the Zinc Corporation for their kindly assistance during the writer's visit to Broken Hill, and for their courtesy in shipping specimens collected at that time; and Mr. Campbell's generosity is deeply appreciated. The writer gratefully acknowledges the opportunities provided for research through the John Simon Guggenheim Memorial Foundation, and a welcome grant from the Shell Research Fund, Stanford, facilitated purchase of equipment.

MANGANPYROSMALITE

Manganpyrosmalite occurs in the form of hexagonal tablets up to 4 mm. in diameter, although they are usually very much smaller than this, attached to the outer surfaces of a long prismatic crystal of clear green ferroan johannsenite, in a manner that lacks any suggestion of epitaxial relationship between the two minerals. Crystals that are about 4 mm. in diameter are about 1 mm. thick, and this ratio of diameter to thickness is generally applicable to crystals of smaller dimensions. In one instance a perfect crystal of manganpyrosmalite, 1.5 mm. in diameter, was observed as a terminal cap to one extremity of a pale flesh-colored acicular crystal of bustamite, that in turn projected outwards at about 80° from a prism face of a crystal of ferroan johannsenite, 9 mm. long. The *c* axis of the manganpyrosmalite is almost parallel to the *b* axis of bustamite, but the angular relationship between bustamite and clinopyroxene does not appear to follow any simple crystallographic scheme.

Crystals 1 mm. thick are quite translucent and pale brown in color. Prism faces give good reflections but the basal plane does not, since the latter is distinctly but shallowly depressed without any suggestion of a spiral development.

Several crystals were carefully removed from the surface of the clinopyroxene and after being coarsely crushed, manganese stain was removed by treatment with SO_2 solution. This material was subsequently analyzed and it is to be regretted that in order to preserve sufficient material for reference purposes it was possible to make a partial analysis only; this is set out in Table 1 together with that of manganpyrosmalite described by Frondel and Bauer (1953, p. 757).

The Broken Hill material is decidedly more manganiferous than that from Sterling Hill, and accordingly, this points to the existence of a more continuous ionic substitution series that extends Frondel and Bauer's observed limits at the manganese end, *viz.* from $\text{Fe}:\text{Mn}=1:3.2$ to $\text{Fe}:\text{Mn}=1:5.7$.

The following physical properties have been determined:

$$\begin{aligned}\epsilon &= 1.631 \pm 0.001, \\ \omega &= 1.670 \pm 0.001, \\ \omega - \epsilon &= 0.039;\end{aligned}$$

Uniaxial and optically negative;

Sp. Gr. at 21° C.=3.12;

A perfect (0001) cleavage.

Employing a camera of 114.59 mm. diameter and manganese-filtered iron-radiation a powder photograph was obtained for a sample of manganpyrosmalite prepared by rolling a thread of the mineral powder bonded with gum tragacanth. The d -spacings are listed in Table 2 together with those recorded by Frondel and Bauer (1953, p. 756), and it will be noted that a few weak reflections have been observed in the film of Broken Hill material that were not recorded by Frondel and Bauer, and *vice versa*. The extra lines present in the former are certainly not due to rhodonite, bustamite, nor johannsenite, and there is every reason to believe that the material used was quite pure. Beta lines for the strongest reflections were found on the film although filtered radiation was employed, but these are not listed.

The intensities [column *I* (2)] compare closely with those for Sterling Hill material but careful examination of the lines on the film reveals a lack of uniform density that points to preferred orientation of the particles in the spindle employed. Short arcs rather than uniform lines were present in a number of instances. A second preparation was formed into a sphere, 0.1 mm. in diameter, without formation of a thread or prelimi-

TABLE 1. ANALYSES OF MANGANPYROSMALITE

	<i>A</i>	<i>B</i>
MnO	39.09	43.44
FeO	12.43	7.65
MgO	0.74	0.89
ZnO	1.94	*
CaO	nil	nil
(Al, Fe) ₂ O ₃	nt.dt.	nil?
SiO ₂	34.13	34.29
As ₂ O ₃	0.13	nt.dt.
Cl	3.80	nt.dt.
H ₂ O	8.18	nt.dt.
	100.44	86.27
O=Cl	0.86	
	99.58	

A. Manganpyrosmalite, Sterling Hill, New Jersey. Frondel and Bauer (1953, p. 757, Table 1).

B. Manganpyrosmalite, South End, 12th Level, Zinc Corporation Mine, Broken Hill, New South Wales, Australia. Anal. C. Osborne Hutton.

* Microchemical tests indicate that this constituent is present.

TABLE 2. X-RAY POWDER FILM DATA FOR MANGANPYROSMALITE
Manganese-Filtered Iron-Radiation, $\lambda = 1.9373 \text{ \AA}$. Intensities Determined Visually

Broken Hill, N. S. W.			Sterling Hill, N. J.		Broken Hill, N. S. W.			Sterling Hill, N. J.	
<i>d</i> . meas.	<i>I</i> (1)	<i>I</i> (2)	<i>d</i> meas.	<i>I</i>	<i>d</i> . meas.	<i>I</i> (1)	<i>I</i> (2)	<i>d</i> . meas.	<i>I</i>
11.57 Å	3	3	11.60 Å	3	1.842 Å	5	3	1.843 Å	4
7.15	8	10	7.16	10	—	—	—	1.790	1*
6.71	1	1	6.71	1	1.765	<1	1*	1.768	1
6.08	3	3	6.09	3	—	—	—	1.733	1*
5.80	1	1	5.77	1	1.710	<1	1*	—	—
4.895	2	2	4.886	2	1.677	6	5	1.672	5
4.52	2	2	4.509	1	1.633	5	4	1.627	4
4.39	2	1	4.376	1	1.525	6	5	1.523	5
3.732	2	2	3.736	2	1.484	<1	1*	—	—
3.58	4	8	3.583	8	1.462	<1	1*	—	—
3.415	3	6	3.419	4	1.431	2	1*	1.432	1
3.335	1	1	3.338	3	1.424	4	3	1.419	2
3.210	4	3	—	—	1.397	1	1	1.406	1*
3.034	2	2	3.035	2	1.372	3	2	1.371	2
3.002	2	2	—	—	1.346	3	2	1.342	2
2.892	2	1	2.882	2	1.284	2	2	1.285	2
2.775	2	1	2.770	2	1.271	1	1*	1.266	1
2.694	10	9	2.683	9	1.242	2*	1*	1.238	1
2.634	<1	1*	—	—	—	—	—	1.194	1
—	—	—	2.549	2	1.128	1*	1*	1.126	2*
2.477	<1	1*	—	—	1.103	2*	1*	1.106	1*
2.384	1	1	2.385	2	1.090	1*	1*	1.089	2*
2.338	<1	1*	2.334	1	—	—	—	1.082	2*
2.252	7	7	2.251	7	—	—	—	1.063	1*
2.092	1	1*	2.102	1*	1.051	1*	1*	—	—
					—	—	—	1.047	1*
					1.032	1*	1*	—	—
					0.999	1*	1*	—	—

I (1) Intensities for film obtained from carefully prepared specimen that lacked any significant orientation of particles.

I (2) Intensities for film obtained from conventionally prepared specimen.

* Diffuse lines, often quite broad.

nary rolling, to prevent orientation of particles, and the x-ray film obtained therefrom exhibited powder lines devoid of uneven distribution of densities; the latter are recorded in column *I* (1), and it is felt that these figures are more acceptable than those in column *I* (2). Accordingly the three most prominent lines in order of decreasing intensities are those with *d*-spacings 2.694, 7.15, and 2.252. Examination of Table 2 will show other differences in intensities between the two patterns.

Rotation and Weissenberg films were secured for manganpyrosmalite and the latter were calibrated with quartz; appropriate measurements gave the following data:

$$\begin{aligned}a_0 &= 13.38\text{\AA} \pm 0.03\text{\AA}. \\c_0 &= 7.15\text{\AA} \pm 0.03\text{\AA}.\end{aligned}$$

These values correspond closely to those obtained by Frondel and Bauer for Sterling Hill, New Jersey manganpyrosmalite, *viz.* $a_0 = 13.36\text{\AA}$ and $c_0 = 7.16\text{\AA}$.

It was noted earlier that in most instances the (0001) faces are shallowly depressed and exhibit at the same time an effect that closely resembles coarse mosaic structure. However, the amount of apparent disorientation of units within a single crystal that is so obvious megascopically is not especially evident in single crystal photographs, since only occasional reflections are slightly dispersed.

BUSTAMITE

Bustamite occurs as very pale, flesh-colored acicular crystals, slightly flattened parallel to the c axis, that project from plates of ferroan johannsenite and manganpyrosmalite. Most of the prisms do not exceed 3 mm. in length and none exceed 1 mm. in the direction of greatest breadth.

The following properties leave no doubt as to the identity of the mineral in question, which has been previously recognized at Broken Hill by a number of authors, among whom are Burrell (1942) and Gustafson *et al.* (1950): $\alpha = 1.686 \pm 0.002$, $\beta = 1.697$, $\gamma = 1.701$, $\gamma - \alpha = 0.015$; $2V = 46^\circ (-)$; this is an average of eight determinations with a range of 44° to 48° ; dispersion is faint with $r < v$. Two good cleavages intersect at 94° and α' makes an angle of 45° *ca.* with (100), assuming that the latter is the better developed of these cleavages. Crystals are flattened prismatic and elongated in the b direction. Specific gravity, determined by suspension in Clerici solution, is 3.42 at 22°C .

When these optical data are plotted on the curves developed by Sundius (1931, p. 513) they are found to correspond closely to moderately lime-poor bustamite with a composition equivalent to 40% (Mn, Fe)SiO₃ and 60% (Ca, Mg)SiO₃; thus it is comparable to a bustamite from Långban described by Otto (1936, p. 112, table 16, 3rd analysis), and very similar to Treburland bustamite described by Tilley (1946, pp. 237-238).

Employing manganese-filtered iron-radiation and a camera of diameter 114.59 mm., x-ray diffraction powder patterns have been obtained for carefully selected bustamite free from manganese oxide films. The d -spacings and estimated intensities are compared with those secured for carefully purified Franklin Furnace bustamite in Table 3, and these patterns are similar, although several lines of comparable d -spacings do

TABLE 3. DATA FROM X-RAY POWDER FILMS FOR BUSTAMITE
Manganese-Filtered Iron-Radiation. $K\alpha = 1.9373 \text{ \AA}$. Intensities Estimated Visually

Broken Hill, N. S. W.		Franklin Furnace, N. J.		Broken Hill, N. S. W.		Franklin Furnace, N. J.	
<i>d.</i> meas.	<i>I</i>	<i>d.</i> meas.	<i>I</i>	<i>d.</i> meas.	<i>I</i>	<i>d.</i> meas.	<i>I</i>
7.29 \AA	1	7.19 \AA	<1	1.915 \AA	2	1.922 \AA	2
6.76	<1	—	—	1.887	<1	1.8845	<1
4.78	<1	4.78	<1	1.852	<1	1.8495	<1
4.35	1	4.49	<1	1.824	<1	1.821	<1
3.88	<1?	—	—	1.775	4	1.776	5
3.675	3	3.70	2	1.746	1	1.7395	1
3.56	1	3.56	1	1.706	5	1.706	2
3.39	3	3.41	2	1.6655	5	1.665	4
3.31	1	3.29	1	1.6555	2	1.6545	2
3.195	7	3.19	5	1.608	<1	1.606	1
3.109	<1	3.096	1	1.552	3*	1.551	2
2.982	6	2.989	6	1.504	1	1.5025	1
2.872	10	2.880	10	1.4785	2*	1.476	1*
2.701	1	2.711	3	1.442	2	1.446	2
2.618	2	2.621	2	1.4325	<1	1.436	3
2.551	1	2.556	<1	1.4210	1	1.424	1
2.5035	1	2.509	2	1.407	2	1.4055	2
2.4545	4	2.462	1	1.3495	2	1.354	2
2.389	3	2.408	2	1.316	3	1.322	2
2.261	2	2.260	2	1.298	3	1.296	2
2.2235	5	2.227	4	1.264	<1	—	—
2.1135	2	2.117	2	1.236	3	1.235	3
2.101	2	2.082	1				
2.020	1	2.016	<1				
1.9535	2	1.956	1				

* Broad and diffuse lines.

not exhibit identical intensities. Notable in this respect is the line at 1.706 \AA . Further it should be noted that ASTM card 3-0693 for bustamite, also from Franklin Furnace, lists 1.78 \AA and 1.67 \AA as the second and third most intense lines, respectively, while it omits many apparently significant lines. The former situation does not apply with either of the bustamites reported upon here.

The diminution of intensities of lines corresponding to 1.78 \AA and 1.67 \AA in either case, would not appear to be the result of preferred orientation in the powdered preparations since several carefully prepared spheres of powder, 0.1 mm. in diameter, and not rolled threads or smeared fibers, were used. Diffraction patterns obtained with the latter, on the other hand, show that the intensity of the line at 1.78 \AA is very

weak in both Broken Hill and Franklin Furnace material, whereas several other lines, sometimes unimportant in films secured from disoriented preparations, exhibit a considerable degree of intensity. Notable in this respect are reflections at 3.195 Å—the most intense lines in films secured from *rolled* spindles of Broken Hill and Franklin Furnace material.

FERROAN JOHANNSENITE

Clinopyroxene forms clear pale green bladed prismatic crystals that are strongly flattened parallel to the *b* axis, and coarsely striated parallel to the *c* axis; all crystals examined were devoid of terminal faces, but surfaces due to parting parallel to (001) are common. Ferroan johannsenite forms the base on which manganpyrosmalite and bustamite have crystallized, and in many instances the surfaces of the pyroxene crystals are obscured by films of deep red-brown sturtite.

The following physical properties have been determined: $\alpha = 1.716 \pm 0.001$, $\beta = 1.728$, $\gamma = 1.745$, $\gamma - \alpha = 0.029$; $2V = 64^\circ \pm 1^\circ (+)$, $Z \wedge c = 48^\circ$. The beta value lies within the narrow limits found for all Broken Hill clinopyroxenes by Burrell (1942) and quoted by Stillwell (1953). No dispersion was observed in suitably oriented interference figures and crystals lying on the dominant face (100) exhibit emergence of very nearly centered optic axis interference figures. The specific gravity at 16° C. is 3.55.

An analysis of the clinopyroxene is set out in Table 4; this shows that the mineral is richer in manganese than it is in iron and not greatly different from the composition of vogtite, a constituent of acid steel-furnace slags (*vide* Hallimond, 1919). However, on account of the higher manganese content it differs quite distinctly from the "green rhodonite" of the Broken Hill lode (Stillwell, 1922, p. 401), a mineral that was later shown to be manganhedenbergite (Hodge-Smith, 1926). If magnesia is distributed equally between theoretical hedenbergite and johannsenite molecules the composition is found to lie nearer that of johannsenite, and accordingly it would seem appropriate to use the term ferroan johannsenite for this pyroxene if one follows Schaller's (1930) nomenclatural recommendations, and the usage of Allen and Fahey (1953). It follows from this that the term manganoan hedenbergite ought to be employed for those pyroxenes in which the hedenbergite molecule is predominant, and the term manganhedenbergite—applied to an indefinite range of manganese-bearing clinopyroxenes—should be dropped.

It is interesting to note that johannsenite is much richer in iron than is bustamite, that is, if the composition of bustamite inferred from physical properties is correct. This suggests that a large excess of manganese would seem to have been available so that when the temperature of the

TABLE 4. FERROAN JOHANNSENITE FROM BROKEN HILL, NEW SOUTH WALES, AUSTRALIA

Anal. C. Osborne Hutton

		Metal atoms on basis of 6 oxygens			mol per cent
SiO ₂	48.39	1.986	2.0	FeSiO ₃	23.05%
Al ₂ O ₃	0.58	0.028		MnSiO ₃	24.55
TiO ₂	nil			MgSiO ₃	6.70
Fe ₂ O ₃	nil?			CaSiO ₃	45.70
FeO	13.44	0.461	2.0		
MnO	14.14	0.491			
MgO	2.19	0.134			
CaO	20.79	0.914			
K ₂ O	0.05				
Na ₂ O	0.09				
H ₂ O ⁺	0.08				
H ₂ O ⁻	0.12				
	99.87				

environment rose above that of the johannsenite-bustamite inversion point (*vide* Bowen, Schairer and Posnjak, 1933, pp. 271, 275), a manganese-rich bustamite was able to crystallize and at a lower temperature than would have obtained for inversion of manganese-poor hedenbergite. This inversion temperature would appear to have been above 830° C. (Schaller, 1938, p. 581), but below 965° C.

Broken Hill johannsenite was heated to 1070° C. for 15½ hours in a silica capillary tube that had been evacuated, filled with nitrogen and then re-evacuated, and the higher temperature was chosen in order that the inversion might proceed and be completed more rapidly. After heat treatment the pyroxene was white or very pale gray in color and the x-ray pattern (Table 5, column B) shows that the mineral had completely inverted to high-temperature manganese-iron wollastonite solid solution, or bustamite, as was to be expected from Bowen, Schairer and Posnjak's (1933, p. 271) study of the system CaO-FeO-SiO₂ (compare columns B, C, and D in Table 5). This experiment was undertaken primarily to check the x-ray powder data recorded by Schiavinato (1953) for bustamite or manganese-rich wollastonite artificially produced by inversion of johannsenite. Schiavinato's (1953, p. 8, Table 2) x-ray data for this inversion product are scarcely comparable to those obtained by the present study, and the smaller number of lines recorded by that investigator is puzzling, as also is the case for his johannsenite.

TABLE 5. X-RAY DATA FOR FERROAN JOHANNSENITE, INVERTED FERROAN JOHANNSENITE, (=BUSTAMITE), BUSTAMITE, AND WOLLASTONITE

Camera diameter=114.59 mm. A, B, and C: Mn-filtered Fe-radiation ($K\alpha=1.9373 \text{ \AA}$)
D: Ni-filtered Cu-radiation ($K\alpha=1.54180 \text{ \AA}$).

A		B		C		D	
d meas.	I	d meas.	I	d meas.	I	d meas.	I
9.18 A	<1	7.34 Å	1	7.29 Å	1	7.67 Å	2
6.55	2	6.76	<1*	6.76	<1	5.03	1
4.75	1	4.82	<1	4.78	<1	4.31	1
4.52	1	4.355	1	4.35	1	3.785	4
3.89	2*	3.87	2*	3.88	<1?	3.685	1
3.335	1}	3.705	2	3.675	3	3.48	4
3.26	2}	3.58	<1	3.56	1	3.36	<1?
3.19	<1?	3.41	3	3.39	3	3.29	4
3.105	<1	3.31	2	3.31	1	3.13	1
3.008	10	3.205	6	3.195	7	3.055	2
2.905	3	3.091	<1	3.109	<1	2.96	10
2.593	5	2.995	5	2.982	6	2.787	2
2.5435	8	2.889	10	2.872	10	2.7055	2
2.346	1	2.700	1	2.701	1	2.54	3
2.234	2	2.6315	2	2.618	2	2.46	5
2.187	<1	2.560	<1	2.551	1	2.335	4
2.156	3	2.5225	1	2.5035	1	2.281	3
2.1235	2	2.471	2	2.4545	4	2.170	6
2.070	2	2.407	3	2.389	3	2.083	<1
2.034	2	2.276	2	2.261	2	2.009	2
2.014	2	2.2345	3	2.2235	5	1.970	1
1.9825	1	2.124	2*	2.1135	2}	1.9075	1
1.892	<1	—	—	2.101	2}	1.874	1
1.8615	<1	2.0275	<1	2.020	1	1.845	<1?
1.833	<1	1.964	1	1.9535	2	1.824	5
1.8102	<1	1.923	1	1.915	2	1.7845	<1
1.7810	4	1.886	<1	1.887	<1	1.7465	4
1.6925	2	1.854	<1	1.852	<1	1.713	7
1.6435	4	1.8255	<1	1.824	<1	1.686	<1?
1.6280	4	1.7805	5	1.775	4	1.652	<1?
1.593	<1	1.752	<1	1.746	1	1.5985	6
1.5745	<1	1.7115	3	1.706	5	1.527	1
1.5505	<1	1.6715	5*	1.6655	5}	1.512	<1
1.537	<1	—	—	1.6555	2}	1.4725	3
1.513	5	1.611	<1	1.608	<1	1.454	3
1.4515	6	1.560	2*	1.552	3*	1.4285	1
1.425	2	1.509	1	1.504	1	1.385	1
1.409	1	1.4815	1*	1.4785	2*	1.358	3
1.355	<1	1.444	2	1.442	2	1.322	1
1.3405	1	?	—	1.4325	<1	1.298	<1
1.3195	<1	?	—	1.4210	1	1.281	<1
1.3000	2	1.415	1	1.407	2	1.265	2
1.2705	2	1.396	1	?	—	1.2385	1
		1.356	1	1.3495	2	1.210	2
		1.3234	2	1.316	3	1.187	1*
		1.3024	1	1.298	3	1.1715	2*
		1.2672	<1	1.264	<1	1.1465	1
		1.2375	1*	1.236	3	1.1395	1
		1.1807	2			1.1115	1
						1.105	2
						1.092	3

A. Ferroan johannsenite, Broken Hill, Australia.

B. Ferroan johannsenite inverted at 1070° C. to manganese-iron wollastonite solid solution (=bustamite).

C. Bustamite, Broken Hill, Australia.

D. Wollastonite, Harrisville, New York.

* Line wide and diffuse.

The d -spacings for inverted Broken Hill johannsenite tend to be very slightly greater than those for the associated bustamite yet the former contains less manganese than the latter. In view of the relative sizes of the ions concerned, *viz.* $\text{Fe}^{2+}=0.75 \text{ \AA}$ and $\text{Mn}^{2+}=0.80 \text{ \AA}$, one might have expected a reversal of this relationship. However, optical properties point to a calcium-poor bustamite, and since calcium is a relatively large ion ($\text{Ca}^{2+}=0.99 \text{ \AA}$) the diminution in d -spacings in the bustamite as compared to those for inverted johannsenite may thus be explained.

It might be pointed out at this stage that the d -spacings for wollastonite recorded by Clark (1946, p. 27) correspond in a general way to those listed in column *D* of Table 5 of this paper, but many significant lines would seem to have been omitted by him, or were not present in his x -ray film. Accordingly since the present author's d -spacings were obtained from a carefully purified powder, prepared for x -ray diffraction work so that preferred orientation of particles would be at a minimum, they are recorded here.

When ferroan johannsenite is heated to 1070°C . for $7\frac{1}{2}$ hours in air the resulting product is black in color and has a magnetic susceptibility that is less than that for the untreated pyroxene. The x -ray powder pattern

TABLE 6. X-RAY FOR FERROAN JOHANNSENITE HEATED TO 1070°C .
FOR $7\frac{1}{2}$ HOURS IN AIR

Manganese-Filtered Iron-Radiation ($K\alpha=1.9373 \text{ \AA}$)

d , meas. \AA	I	d , meas. \AA	I
7.50	1	2.306	3
5.20	<1?	2.251	3
4.89	2	2.149	3
4.48	1	2.116	3
4.24	1	1.980	<1
4.055	7	1.9525	1
3.76	2	1.803	4
3.44	3	1.7295	3
3.33	2	1.686	4
3.25	5	1.632	3
3.044	3	1.603	2
2.989	1	1.579	3
2.922	10	1.522	1
2.751	<1?	1.500	4
2.6885	3	1.455	2
2.555	8	1.431	1
2.508	1	1.372	2*
2.437	4	1.340	2*

* Very diffuse line.

obtained for this material exhibits only the slightest resemblance to the spacings and intensities reported in column *B* of Table 5, presumably as a consequence of oxidation of both iron and manganese (Table 6).

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MEMORIAL OF SHUKUSUKÉ KÔZU

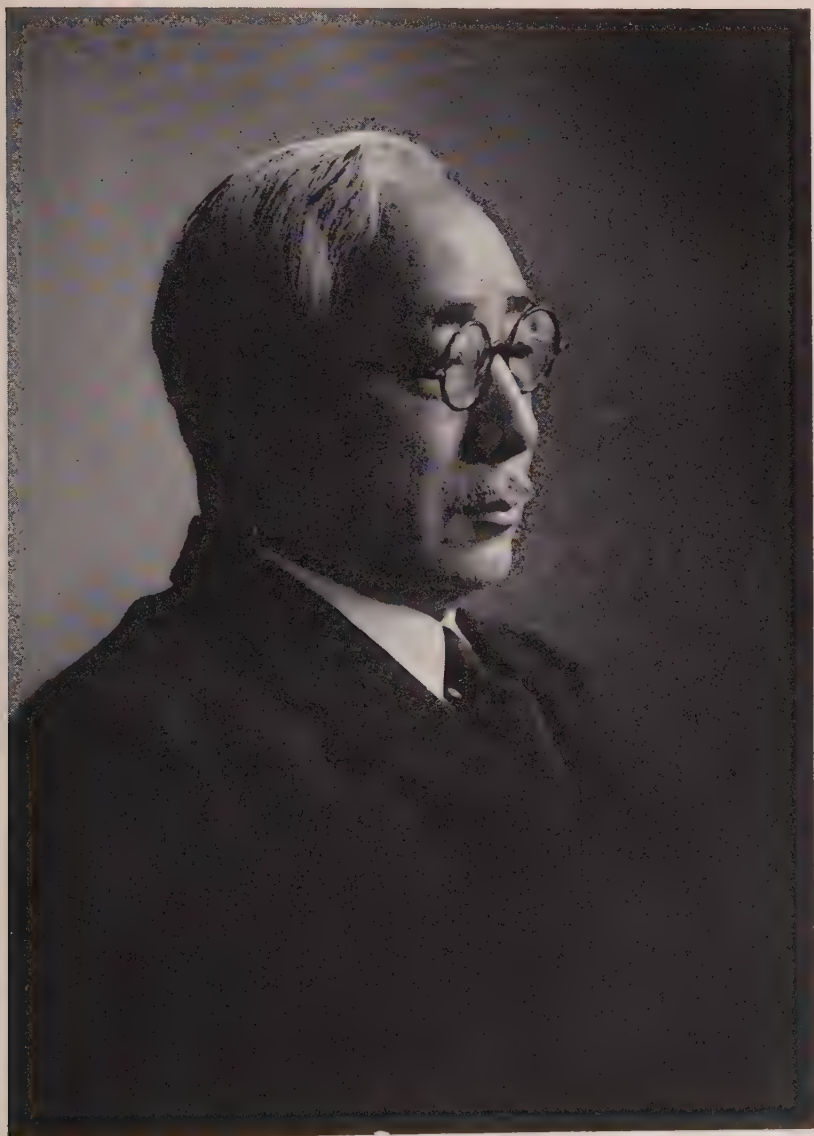
KENZO YAGI, *Tohoku University, Sendai, Japan.*

With the death of Dr. Shukusuké Kôzu, Professor Emeritus of Tohoku University on February 11, 1955, Japan lost one of the most prominent leaders in the field of mineralogy and petrology.

Prof. Kôzu was born on June 5, 1880, as the second son of a famous and wealthy family in Shiga Village, Nagano Prefecture in Central Japan. In 1902 he enrolled at the Imperial University of Tokyo (now University of Tokyo), where he studied geology under Professors B. Koto, K. Jimbo, and M. Yokoyama. Under the stimulating influence of Prof. Koto, who was the founder of petrology in Japan, he also became interested in petrology, and this interest determined his career. During the summer of 1904 he made a geological survey of the volcano Ontake in Central Japan, and in the following summer, 1905, he studied the volcano Norikura, which lies to the north of Ontake. In those days these high peaks (Ontake: 3063 m., Norikura: 3026 m. above the sea level) had few trails and very limited facilities, so he was obliged to camp for several weeks on the tops of these volcanoes, and to make topographic maps by himself. Upon graduation from the University of Tokyo in July 1905, he took a post-graduate course in petrology, and completed his thesis on these two volcanoes. They were later published as Reports No. 59 and No. 71, respectively, of the Earthquake Investigation Committee of Japan. These reports indicated his high ability as a volcanologist as well as a petrologist.

In 1907 he was appointed geologist of the Imperial Geological Survey (now Geological Survey of Japan) in Tokyo. While making his geological survey for sheet maps of Matsuyama, Hiroshima, and Fukae (spelled also Fukue), he found a basaltic rock with alkali feldspar, which had petrographic features similar to mugearite. Following the usual custom in descriptive petrography of that day, he named it "Fukaeite" after the name of the locality. Following this first discovery of alkalic rocks, he became interested in these rock groups like many other petrologists, and found various types of alkalic rocks from numerous localities in Northern Kyushu and Western Honshu of Japan and Korea. In so doing, Prof. Kôzu made a notable contribution to petrology, for up to that time no alkalic rocks had been known in Eastern Asia, and the region was considered as a typical petrographic province of the so-called Pacific type.

In 1911 he was appointed as lecturer of petrology at the University of Tokyo, and in the following year as lecturer at Tohoku Imperial University (now Tohoku University) in Sendai, the Geological Department of



SHUKUSUKÉ Kôzu
1880-1955

which was established in that year. He left Japan in January 1913 for study in America and Europe. First he went to Washington, D. C., and studied at the Geophysical Laboratory of Carnegie Institution of Washington, where he was deeply impressed by the new technique of high

temperature research on silicates, employed at the Laboratory. He made optical and thermal studies on the alkalic rocks and anorthite crystals from Japan. Later the knowledge and experience he obtained there helped him considerably. During his stay of more than a year at the Laboratory he became a close friend of Dr. H. S. Washington, with whom he had an opportunity to make a pleasant trip to Vesuvius and Stromboli in Italy in July 1914. Their friendship lasted until Washington's death in January 1934. In May 1914 he left the Laboratory for Europe.

Owing to the outbreak of the World War I he changed his original plan to study in Germany and Austria, and went to England instead. He studied at the University of Cambridge, under the guidance of Prof. Hutchinson, making a special study of the optical properties of feldspars. At this period his researches on the alkalic rocks of Dogo Island, and many other parts of Japan, as well as some anorthite crystals from Japan were published in the *Journal of Geology* (1911-13) and *Science Reports of Tohoku University, Series II* (1913-14) and his detailed description of the dispersion of the optic axes of alkali feldspars was reported in the *Mineralogical Magazine* (1915-16). Through these papers his reputation as a petrologist was firmly established. He went to Paris in 1916, where he stayed at the University of Sorbonne, and then returned to the United States, again paying a short visit to the Geophysical Laboratory.

Upon completion of his study abroad, which had taken more than three years, he came back to Sendai in July 1916, and was appointed as Professor of Mineralogy and Petrology at Tohoku University, the position which he held until his official retirement in March 1942. After his return to the University, his main interest shifted from alkalic rocks to the studies of thermal behavior in igneous rocks and their rock-forming minerals. He had held a strong opinion that physico-chemical principles should be applied for the solution of genesis of rocks and minerals. Thus the distinction between petrology and mineralogy on the one hand, and geology and paleontology, which had more intimate relation with biology on the other hand, became apparent. Therefore Prof. Kôzu and Prof. Yabe, then Head of the Geological Department of Tohoku University discussed the situation, and reached a conclusion that the Department should be divided into two independent institutes, i.e., the one of geology and paleontology, and the other of mineralogy and petrology. As the result the Institute of Mineralogy, Petrology, and Economic Geology was established in 1921, and ever since he served as Head of the Institute.

In this newly established Institute, Prof. Kôzu and his co-workers

made various experiments on such rock-forming minerals as feldspars, pyroxenes, amphiboles, micas, and zeolites. Not only ordinary optical methods and chemical analyses, but differential thermal analyses, quenching methods, and x-ray photographs, all of which were quite new techniques at that time, were employed in their study. Indeed he was the pioneer in Japan who introduced these methods to the study of rocks and minerals, and in so doing he advanced the knowledge of his contemporaries. During his x-ray study on moonstone from Korea with Dr. Y. Endo in 1921, he found that the double spots in the Laue photographs of a feldspar observed at lower temperatures became single spots upon heating, and thus he could demonstrate for the first time the existence of an exsolution phenomena in silicate solid solutions. Professor Niggli called this research the foundation of "Kristallpathologie," and the work has been referred to in many books and papers dealing with the physico-chemistry of silicates. This may be considered as Prof. Kôzu's second notable contribution and will remain a classic in this field. All these papers were published in the *Science Reports of Tohoku University, Series III* (1921-29).

In 1929 he attended the Pacific Science Congress held in Java, and presented papers on these researches. When he returned from this trip, the volcano Komagatake in Hokkaido erupted violently after a long period of dormancy. Soon after this eruption he and his co-workers made a detailed survey of the activity. In 1930 he made his second visit to Europe and attended the International Union of Geophysics held at Stockholm in August 1930. The results of their survey of Komagatake were presented at this Union, and were later published in a *Memoir of Saito Hôonkai* (1932) and *Tschermak's Mineralogische und Petrographische Mitteilungen* (1934).

At that time the Geological Society of Japan was the only society concerned with the geology in Japan, and its Journal had not enough space to publish numerous papers on mineralogy and petrology. Therefore he took the initiative to establish a new society for the development of mineralogy and petrology. In 1929 the Japanese Association of Mineralogists, Petrologists, and Economic Geologists was founded and he was elected President of the Association, which position he retained until his death in 1955. Nearly every number of the Journal of this Association contained contributions by him and his co-workers covering a wide scope of petrology and mineralogy, and the Journal has served as a leading publication in this field in Japan.

For his meritorious achievement in thermal research of rock-forming minerals, the Imperial Academy (now the Japan Academy) voted in 1932 to award him the Academy Prize. In the same year he was also

elected to the Academy. As a consequence he never actually received the prize, because of a rule of the Academy that a member could not be a recipient of its prize. He made numerous contributions also to the Proceedings of the Academy thereafter.

After his long and distinguished service of thirty years at the University, he retired from teaching in March 1942 at the age of sixty-one, and became Professor Emeritus of Tohoku University. Subsequently he moved to Tokyo, where he was active as a member of the Academy as well as the Chairman of the Committee for Exploration of Rare Element Minerals. In 1944 he went to Korea to study such minerals. In the following year his residence was unfortunately burned by an air raid and he moved back to his native home in Shiga Village, Nagano Prefecture. He and his co-workers made a geological survey in the vicinity of the village, which lies immediately south of the famous volcano Asama. The result of this joint study was recently published as a posthumous work (*Geology of Kitasaku Province*). In 1951 as a former visiting investigator at the Geophysical Laboratory he contributed for the Bowen volume a paper on the Japanese twins of quartz, a subject in which he had been interested for many years.

Professor Kôzu was a member or a fellow of many scientific societies both here and abroad. He served as Vice-President of the Volcanological Society of Japan (1931-45), President of the Geological Society of Japan (1938-39), and President of the Japanese Association of Mineralogists, Petrologists, and Economic Geologists (1929-55).

When young, Professor Kôzu possessed such good health that he could camp out on the high peaks for many weeks, but he developed tuberculosis during his stay in Paris, and later suffered from heart disease and other physical disabilities. When he became professor, he was a bachelor and lived in his laboratory at the Tohoku University. In spite of his poor health, he used to work on his experiments, often until midnight, and then go to sleep on his "bed" which was a pile of large wooden sample boxes in the corner of his laboratory. It was often said that he conquered his illness by his strong will. However, after a critical illness in 1951, his health continued to decline until he passed away in 1955 from general weakness at the age of seventy-four at his new residence in Kamakura.

Professor Kôzu's publications number nearly 260 and most of the papers since 1920 are joint works with his associates. They are all characterized by accurate data on optical, chemical, and thermal properties of rock-forming minerals, and the application of the principles of physico-chemistry to the understanding and genesis of igneous rocks.

As a man, Professor Kôzu was very honest and sincere. As a teacher,

he gave inspiring lectures to arouse in his students an intense and abiding interest in rocks and rock-forming minerals. His ability as a leader was indeed remarkable. His sincere and vigorous attitude toward his study was highly respected by his co-workers, his students, and all who came in contact with him. As he possessed poor health he had little interest in outdoor sports, but instead had various other hobbies, such as playing *go* (Japanese chess), singing *utai* (chanting of Japanese traditional drama text), collecting Japanese paintings, and potted plants of pine and azalea. Such was his enthusiasm even in these cases, that the wide garden of his residence in Sendai was filled with hundreds of potted pine plants. His most favorite "hobby," however, was the study of rock-forming minerals, to which he devoted his entire life.

ORIGIN OF AUTHIGENIC INCLUSIONS IN SYNTHETIC CRYSTALS

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ABSTRACT

Authigenic inclusions in natural crystals and crystals grown in the laboratory are described. Detailed description of the laboratory growth of ammonium dihydrogen phosphate is made to illustrate the development of inclusions during growth. It is suggested that these inclusions both in natural and synthetic crystals have their origin in some interruption of the growth process.

Visible inclusions are common optical defects of both natural and synthetic crystals. The term "inclusion" is given to any foreign body either solid, liquid or gas inclosed within the crystal.¹ One can recognize two classes of inclusions: primary—those inclusions associated with the growth of the crystal, and secondary—those inclusions which form after growth.²

Specific terms are used in the literature to describe the various forms of inclusions:³

- (a) Bubbles (Gordon, p. 284)—bubble shaped cavities of various sizes filled with vapor or solution.
- (b) Negative crystals (Ford, p. 201)—cavities having definite crystal shape.
- (c) Veils (Gordon)—thin sheets of small inclusions.
- (d) Phantoms or ghosts (Gordon, Johnston)—"oriented veils" (an envelope of planar veils each one of which is parallel to some possible crystal face usually, but not always, identical with the final crystal).
- (e) Clouds—aggregates of fine bubbles or cavities.
- (f) Solid crystals or mineral fragments—the included crystals may be:
 - (1) Foreign matter suspended in the mother liquor which is incorporated and overgrown, e.g., clay or chlorite in quartz (Johnston).
 - (2) Phases exsolved after growth is complete, e.g., bronzite (oriented ilmenite inclusions).
 - (3) From crystals that crystallize out of included mother liquor, e.g., NaCl in quartz vacuoles.

Although the inclusions sometimes occur in irregular arrangement (1, p. 202), more commonly they exhibit a definite orientation with respect to some common crystallographic direction. For example, the phan-

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¹ Ford, W. E., *Dana's Textbook of Mineralogy*, 4th Ed., p. 222, Wiley, N. Y., 1932.

² Laemmlein, G., *Zeit. Krist.*, **71**, 237-256 (1929) (41 references).

³ Gordon, S. G., *Am. Mineral.*, **30** (5, 6), 284-285 (1945). Johnston, W. D., Jr., and Butler, K. D., *Bull. Geol. Soc. Am.*, **57**, 601-650 (1946).

toms in quartz where bubbles or mineral grains are arranged in a series of thin planes each one of which is parallel to some rhombohedral termination. Since the termination of such a crystal as quartz is related to the directions of most rapid growth, it is obvious that the phantom also reflects a stage in the growth process.

It must be recognized that some inclusions are probably post-growth (secondary) and are derived from local resolution, exsolution or chemical alteration. Examples of these are: nepheline (elaeolite) which has an oily or greasy luster probably due to oriented unmixed inclusion since pure nepheline is vitreous in luster,⁴ and bronzite which owes its bronze sheen to exsolved thin plates of ilmenite.⁴

Phantoms or veils have been observed in the following crystals:

TABLE 1. ORIENTED AUTHIGENIC INCLUSIONS IN NATURAL CRYSTALS^{2,3}

Mineral	System	Orientation
Quartz	Trig.	to prism ⁵
Beryl	Hex.	Hexagonal tubes to c ⁵ (negative crystals) also to prism
Diamond	Cubic	to (111) (110) ⁶ Clouds to (110)
Barite	Ortho.	to (110), (102), (210) ⁷
Gypsum	Mono.	to prism edge
Corundum	Hex.	1011 and 1120
Fluorite	Cubic	to (111)
Calcite	Trig.	to cleavage

Inclusions usually form during the growth when the rapidly growing crystal incloses mother liquor or other phases, either growing simultaneously, or introduced from outside the growth chamber. With slow growth the growing crystal usually rejects impurities ahead of the growing face resulting in a corresponding higher perfection. Interruption of growth may lead to inclusions as will be shown later. The self-purification during growth concentrates the impurities in the residual mother liquor until eventually they may precipitate, as illustrated in the pipe of a steel ingot or the center of an ice cube.

It will best serve our purpose to limit the discussion to authigenic inclusions of solution or vapor formed during the growth process since those are best illustrated by laboratory data.

⁴ Ramdohr, R., Klochmann's Lehrbuch der Mineralogie, 13th ed., Enke, Stuttgart, p. 221 (1948).

⁵ Cameron, E. N., *et al.*, *Am. Mineral.*, **38**, 218-262 (1953).

⁶ Gubelin, E., *Schweiz. Min. Petr. Mitt.*, **28** (1), 146-156 (1948).

⁷ Whitlock, H. P., Report. Dir. N. Y. State Museum, p. 163 (1917).

No over-all generalization about the veiling tendency among various crystals can be made since it is definitely related to the habit of the crystal. Crystals show varying degrees of habit modification. For example, *ADP* ($\text{NH}_4\text{H}_2\text{PO}_4$) rarely shows more than two forms. More than fifty forms have been reported for quartz. During the growth of the crystal the solution composition (which dominates the habit) may change. Thus the phantom may not contain all of the forms shown by the final crystal. Independent of the degree of variation of habit the

TABLE 2. ORIENTED AUTHIGENIC INCLUSIONS IN SYNTHETIC CRYSTALS

Formula	System	Orientation
$\text{LiSO}_4 \cdot \text{H}_2\text{O}$	Mono.	\parallel to (110)
NH_4Cl	Cubic	\parallel to (100) (tubes)
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Triclinic	
$\text{NH}_4\text{H}_2\text{PO}_4$ (ADP)		
KH_2PO_4	Tetr.	\parallel to (101)
KH_2AsO_4		
Rochelle Salt	Ortho.	
NaCl	Cubic	\parallel to 100
NaBrO_3	Cubic	\parallel to (-111)
NaClO_3	Cubic	\parallel to (100)
KClO_3	Tetr.	\parallel to (100)
CaF_2	Cubic	\parallel to (111)
Alum	Cubic	\parallel to (111)

phantom or veil usually contains only the lower index forms and rarely shows the vicinal forms common to the final crystal.

There are several synthetic crystals which may occasionally grow without trace of a veil on the seed, e.g., HIO_3 , quartz, and alum. In each case the solutions from which these crystals grow are of high concentration (high solubility) and show a high tendency to supersaturate. From a practical viewpoint the crystal grower can state that the "ease of growth" for these crystals is high.

The habit of a crystal is fixed to a high degree by the internal structure but can show some variation depending upon the environment during growth. One can modify the habit in some crystals within wide limits by changing the environment. For example, too rapid growth with poor agitation may yield dendrites or spherulites—incomplete crystals. The effect of pH is notable in the case of $\text{NH}_4\text{H}_2\text{PO}_4$ where growth is limited to the *c*-axis direction for low pH 4.0, but also takes place in the *a*-axis direction when the pH exceeds 6.0.

For each environment there appears to be maximum rate of growth which if exceeded results in poor crystals. As shown by numerous ex-

periments this optimum rate is also a function of crystal size⁸ both at the microscopic and macroscopic level.

An examination of the work of Groth⁹ and Buckley¹⁰ will show there are many instances demonstrating habit modification by change of solution composition. As yet no satisfactory correlation of these data is available.

If we examine the state of affairs during crystal growth we find we are dealing with a solid-liquid equilibrium. The solid is in some sort of equilibrium with the saturated solution—a liquid. However, the saturated solution may be regarded as an attenuated solid. There is some evidence that already in the supersaturated solution there is some preorganization of material directed toward the crystalline state, e.g., HIO_3 where dimers and trimers are found in the saturated solution.¹¹

Speculating further, it is reasonable to assume that addition of some foreign ion would influence the solution and the preorganization for the following reasons: (a) The effect of addition is out of all proportion to the amount of the addition, 1% has a high effect. (b) The active habit-modifying impurities are preferentially absorbed. These impurities are also incorporated in the structure up to the saturation value (in $\text{NaCl}-\text{PbCl}_2$ system this is of the order of 5×10^{-4} mol % Pb^{++}).

As Wells¹² and others have pointed out, for each environment (solution) there is a characteristic set of endforms. If a crystal is shifted from one environment to another the new set of endforms is assumed. If we place two crystals with different endforms in the same environment (solution), nothing happens (the energy difference for macroscopic crystals of different face assemblage is too small) until growth is permitted whereupon both crystals assume the form characteristic of the solution.

If an anhedral fragment is allowed to grow, it will rapidly assume the equilibrium form but in so doing the interface between seed and new growth is usually cloudy or veiled. The relations between habit, seed, and veiling are well illustrated with the laboratory growth of ammonium dihydrogen phosphate.

THE LABORATORY GROWTH OF AMMONIUM DIHYDROGEN PHOSPHATE (ADP)

Ammonium dihydrogen phosphate (ADP) crystallizes in the tetragonal scalenohedral class of the tetragonal system. Its habit comprises

⁸ Egli, P. H., and Zerfoss, S., *Discussions Farad. Soc.*, No. 5, 61–66 (1949).

⁹ Groth, P., *Chemische Kristallographie*, Leipzig, W. Engelmann (1908).

¹⁰ Buckley, H. E., *Crystal Growth*, N. Y., Wiley (1951).

¹¹ Sidgwich, *Chemical Elements and Their Compounds*, Vol. 2, p. 1228, Oxford Press (1950).

Nayar, M. R., and Srivasta, L. N., *Phil. Mag.*, **39**, 800–805 (1948).

¹² Wells, A. F., *Phil. Mag.*, **37**, 184–199 (1946).

two forms, the second order prism (100) and the second order tetragonal bipyramid (101) (9, Vol. 2, p. 796). Groth does not report the basal pinacoid (001) as a form nor does it occur in the related potassium phosphates and arsenates. Growth from water solution is generally along the *c*-axis ($\text{pH}=4$). However, thickening along the *a*-axis can be obtained by making the solution more basic ($\text{pH}=6$).

Commercial production of *ADP* single crystals (2–3 pounds) takes place in two stages: (1) the production of a cap (equilibrium seed) from a seed plate, and (2) growth of the final crystal from the cap. Commercially both operations are done by a temperature-lowering operation rather than by the less easily controllable constant temperature evaporation method (Plate 1A).

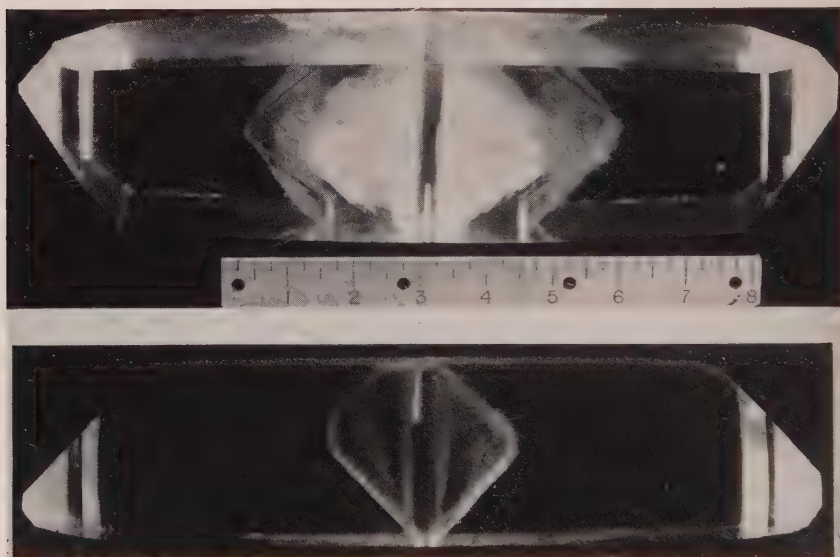


PLATE 1. A. Ammonium dihydrogen phosphate (*ADP*) crystal grown from a cap by temperature lowering. The cap was grown from a seed plate cut parallel to 001. B. *ADP* grown from a "synthetic" cap. (Scale units in inches.)

In the first or capping operation a *Z*-cut plate (plate parallel to 001) is placed in a solution saturated at 50°C . and rapidly grown by temperature lowering into the doubly terminated (but cloudy) cap.

The various successive stages in the capping operation are shown in Fig. 1. Growth first takes place on the 8 corners of the two large faces of the seed plate (in the *Z*-direction) in the form of small pyramids. These pyramids gradually expand along the edges and in the *Z*-direction until they touch. If the capping operation is carried out sufficiently rapid,

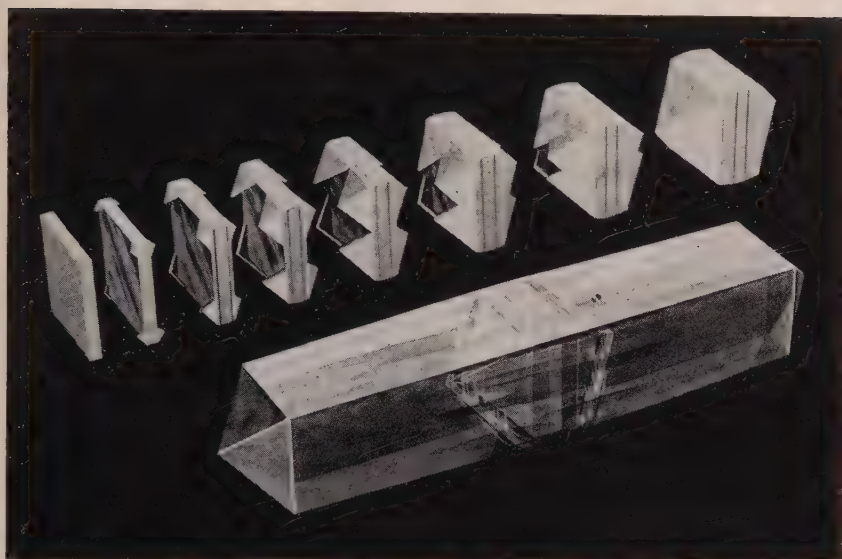


FIG. 1. Stages in the capping operation of a 001 seed plate of *ADP*.

the pyramids eventually coalesce into a doubly terminated crystal. If the capping operation is too slow the pyramids end up as parallel growth forms.*

Growth on the central portion of the original seed surfaces is incomplete as far as filling out the volume. The cap is usually hollow on both sides of the seed plate and contains solution in the cavity. Poor diffusion *within* the central portion of the seed surfaces during the rapid capping accounts for the failure to complete the crystal interior.

The specification for the initial seed plates requires only that the edges (where growth takes place) be as perfect and unstrained as possible. The condition of the portion of the surface of the seed within the edge is unimportant; in fact the seed can be a "square-toroid."

The growth of the final crystal then proceeds from the cap in a second operation. The cap is planted in a solution saturated at 50° C. With appropriate agitation the solution and cap are allowed to cool to room temperature in a sealed container at a rate of 0.5°/day.

The interface between the cap and new growth also shows a cloudiness or veil that has the shape of the cap. Occasionally during the growth of the main crystal or bar stock thin planar veils perfectly parallel to each

* If the capping is done on crystals mounted on a seed tree which is rotated in the solution with the *c*-axis on the direction of rotation, the front face may cap over nicely while the trailing face may show parallel growth for low speeds of rotation. If the rate of rotation is increased or the direction is reversed at intervals this defect is corrected.

of the four terminal faces (101) may appear. One such crystal is shown in Plate 2. Complete phantoms occur in *ADP* only when growth along the *a*-axis is permitted.

These veils appear as planes of bubbles parallel to a pyramid face. The veil may be a single plane or a series of parallel planes separated by clear material. The veil may be a complete "phantom" of four planes

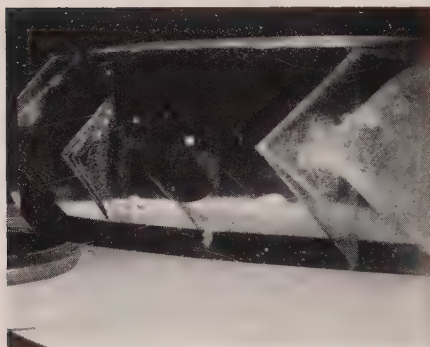


PLATE 2. Repeated veils in *ADP*.

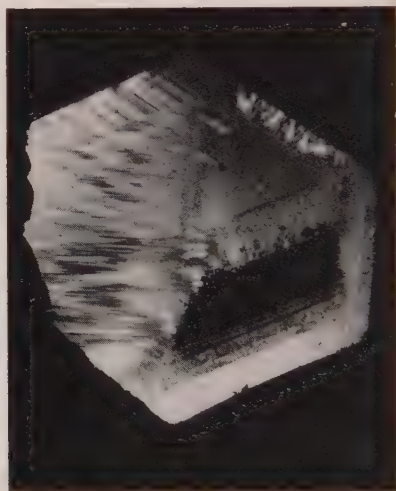


PLATE 3. Basal section of quartz between crossed polaroids showing two growth stages separated by a veil.

arranged pyramidally or only a faint incomplete plane. The veil consists of round or elongated bubbles or tubes with their long axis parallel to a line made by the prism-pyramid intersection. The contents of these bubbles have not been determined.

Two types of veils or inclusions are recognized—those formed during capping and those formed during growth of the main crystal. Both types of veils have a common origin as will be shown.

The transition from seed to cap is illustrated in Fig. 1. This is in reality the transition from a non-equilibrium endform to the endform in equilibrium with this particular environment (solution). Since *ADP* does not exhibit the base 001 as a part of the endform, the use of the basal cut as seed is responsible for the intensive veiling and inclusion during the capping operation.

One step, in line with the theory of endform equilibrium, can be taken to reduce the initial veiling and increase the yield of useful material. This step involves planting a "synthetic" cap—one ground out of clear

oriented material to simulate the one obtained by the capping of a seed plate.* The initial success of this refinement is shown in Plate 1B. It will be noted that the veiling is reduced to a minimum for the synthetic cap.

If we compare the growth into bar stock from the ordinary and synthetic caps there are the following differences:

- (a) The ease of growth as reflected by the degree of control required is much greater for the synthetic cap.
- (b) Almost invariably the ordinary caps induce a major veil at the interface and fine veils within the first 5 mm. of the new material. In part this might be explained on the basis that the ordinary cap is a smooth faced crystal while the synthetic cap has ground (hence more active) surfaces.
- (c) Incidentally one step in the operation is eliminated. From a theoretical point of view the synthetic cap is simply the optimum choice of seed.

Veils that occur during the bar growth have been attributed to supersaturation differences across the face, poor temperature control or inadequacy of the solution circulation.¹³ Concerning the origin of these veils "The temperature must be controlled with considerable precision. Throughout the growth process sudden drops of even 0.1° are likely to cause flaws from too rapid growth and a temperature rise of $0.3\text{--}0.5^{\circ}$ is likely to cause the crystal to redissolve and leave a ghost at that point when growth is resumed."

The two veils or flaws mentioned above differ only in their relative position within the crystal—a temperature drop gives an internal veil while a temperature rise gives a veil originating at the prism edge because of the rounding of the prism—pyramid intersection through solution. Both veils are, of course, parallel to the corresponding faces of the termination.

The laboratory grown crystal previously described and illustrated (Plate 2), with repeated veils at approximate weekly intervals, re-emphasizes the cause of veiling—that of an interruption or a change in the rate of growth over a weekend. In a large laboratory plant, the daily and hourly voltage variations may change abruptly in the heating of the growth apparatus. Similar changes in the humidity delivered by air-conditioning apparatus may produce some effect on crystals grown by evaporation. If one removes a growing crystal from solution and then replaces it after a five minute exposure to air, a flaw usually results. It is the interruption or change in rate of growth that is responsible for these fine veils. The crystal material on either side of the veil interface is in optical continuity. During the act of veiling the growth is so rapid

* Slawson, S. I., U. S. Patent No. 2,543,071 (2/27/51).

¹³ Holden, A. N., *Discussion Farad. Soc.*, No. 5, 312 (1949). Walker, A. C., *J. Franklin Inst.*, 250, 490–492 (1950). Robinson, A. E., *Discussion Farad Soc.*, No. 5, 319 (1949).

that only a part of the face grows over completely. Growth is completed by the coalescence of these growth tendrils with the resulting inclusion of mother liquor. A similar situation would hold if suddenly a shower of foreign particles covered the growing face. As growth, interrupted by this shower, resumed, the particles would be included on a crystal plane as a veil.

Veiling in Other Crystals

Numerous examples of veils and phantoms in natural quartz have been reported. Johnston¹⁴ has described fluid inclusions (veils) in vein quartz. He recognizes two types of arrangement for these fluid inclusions—"(1) in parallel planes determined by the crystallographic directions of the including crystal giving zonal growth lines and (2) in roughly parallel planes which are more or less independent of crystallographic direction and extend across adjacent crystals." Johnston ascribes the origin of type (1) to inclusion during growth and type (2) to post-growth events—possibly cracking and rehealing.

Johnston and Butler³ have described phantoms in Brazilian quartz. These phantoms are either mineral or vacuole in character. They consist of complete or incomplete, single or multiple planes of veils parallel to the various faces of the final crystal. The phantoms do not necessarily show all of the forms of the final crystal nor do they always reflect the tapering (oscillation growth) of the final crystal.

Generally the material beyond the phantom is more likely to exhibit twinning than the material within the phantom. In Plate 3 is shown a basal slice of a Brazilian quartz crystal (Minas Geraes), photographed between crossed polaroids, illustrating the above statement.* The material within the phantom has a uniform polarization color while material outside the veil envelope is badly twinned or at least shows a low degree of perfection.

The critical growth rate for a crystal (the maximum rate at which a crystal can be grown without developing flaws) is an inverse function of size; the larger the crystal the slower the critical rate.⁸ The outer hull of these crystals containing phantoms presumably grew at too fast a rate.

One common observation about quartz crystals is that the crystals are cloudy at the point of attachment or base of the crystal and may get clear toward the apex end. Milky crystals may yield clear material in the rhombohedral zone.³ These clouds of inclusions are akin to the cloudy

¹⁴ Johnston, W. D., Jr., The gold quartz veins of Grass Valley, California: *U.S.G.S. Prof Paper* 194 (1940), plate 21, pp. 42-43.

* From a crystal supplied by W. D. Johnston, Jr., U.S.G.S.

zone in the caps of *ADP*. In beryl it is common to find hollow tubes (negative crystals) parallel to the *c*-axis at the base of the crystals.

The case of veiling in NaBrO_3 is of special interest. Sodium bromate is an apparent exception to the rule that anhydrous salts have low water solubility and grow with difficulty. It is quite soluble in water and grows with ease. Commonly it exhibits a tetrahedral habit modified by the negative tetrahedron and the hexahedron. Over a period of three years using the same solution, large crystals (4") of NaBrO_3 were grown, marred however, by multiple veils parallel to (-111) . Attempts to eliminate the veils by change of pH were unsuccessful.

These veils could be minimized by change of seed cut from 111 to 100 (which meant displacement and confinement of the veil rather than elimination). Analysis showed that the solution contains several per cent of Ca-ion. After this Ca-ion was eliminated the crystals grew clear and unflawed. Further studies in progress should provide an explanation for the influence of this effect.

Conclusions

The occurrence of veils (oriented inclusions or defects) in natural and synthetic crystals has been described. The orientation of the veil is related to the growth process. The veil represents an interruption in the growth process or indicates discontinuity in the growth rate curve.

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FURTHER DATA ON THE STILPNOMELANÉ MINERAL GROUP

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ABSTRACT

Three new stilpnomelane analyses are reported together with their physical data. One of the minerals was separated from quartzose schists and the other two, which exhibited zonary relationship, had crystallized in a glaucophanic mineral assemblage. Using unit cell dimensions determined by Gruner, tentative empirical cell contents for these stilpnomelanes have been calculated, and a figure of 30 oxygens per unit cell appears most probable. The compositions of the minerals are intermediate to those previously recorded and the optical and chemical data determined allow preparation of somewhat better composition refractive index curves than those recorded earlier (Hutton, 1938, 1945). The modes of occurrence in both instances in plumose aggregates and vein-fillings that uninterruptedly traverse foliation, microfolds, and other structural features, point to a very late period of crystallization.

OCCURRENCE AND PETROGRAPHY

*San Juan Bautista Mine, California.** So far as the writer is aware stilpnomelane has not been recorded as such in rocks from the Oak Hill environment by earlier workers, among whom are Carey and Miller (1907), Templeton (1912), and Crittenden (1949, 1951), but it should be made clear that Carey and Miller (1907, pp 167-168) did note the presence of what they believed to be mica—some of which was pale brown in color—in glaucophane schists at this locality, whereas Templeton (1912, pp. 17-18) recorded an abundance of mica but did not mention the color thereof. Although members of the stilpnomelane group of minerals have often been incorrectly identified as biotite—and correct diagnosis may be difficult if grain-size is small—it is not possible to say that this may have been the case so far as Carey and Miller and others are concerned because of the paucity of mineralogical description.

Although Crittenden (1949, pp. 94-95) did not find stilpnomelane in the mineral assemblage of schists from Oak Hill, he (1949, pp. 99, 103) does record it in a metachert and a glaucophane-bearing rock from the nearby Los Buellis Hills area. However, the properties recorded by him for stilpnomelane in the metachert are quite anomalous since although refractive indices are very high, *viz.* $\alpha=1.75$ and $\gamma=1.78$, birefringence is abnormally low, *viz.* 0.03. Crittenden considers that his data, although they differ notably from any previously published by the present writer (Hutton, 1938), are similar to those determined by Larsen and recorded by Winchell (1933, p. 435) for a stilpnomelane from New York. Actually Winchell records no such data!

* Also known as the Hillsdale Mine, 3-4 miles south-east of San Jose, Santa Clara County, California.

Stilpnomelane occurs as a major constituent of both quartzose and albitic glaucophanic schists at the San Juan Bautista Mine. Garnet and sphene are minor accessories whereas clinozoisite, apatite, muscovite, and chlorite are only occasional constituents. Water-clear quartz and often patchily twinned plagioclase occur in cataclastically deformed xenoblastic grains, 1.0 mm. in diameter, and the latter mineral consistently has a composition of An_{9-10} .

Amphibole forms about 15–20% of the rocks and might best be described as a member of the glaucophane-riebeckite series rather closer to glaucophane than to the alkali and iron-rich varieties, on account of pleochroism, small optic axial angles, and medium birefringence. The dominant glaucophanic phase is strongly zoned, especially in the albite-rich rocks, by a second member of the series which differs from the first in two ways, *viz.* (1) more intense absorption but similar pleochroism, and (2) smaller optic axial angle. This suggests that the composition is rather close to that of crossite, but no instance of a transverse optic axial plane was observed.

Stilpnomelane forms plumose and closely interlaminated aggregates with no obvious orientation, and platelets are found to lie at any angle with respect to foliation and schistosity; instances can be found where the radiating crystals stab through albite in more or less continuous fashion (Fig. 1). From a survey of many thin sections it is clear that the color of the stilpnomelane exhibits a distinct range from brown to intense red-brown for the *Z*-vibration direction of the ellipsoid, and in a few instances a range of color was evident within a single sheaf-like aggregate of platelets. Accordingly an attempt was made to determine the compositional range therein by chemical analysis.

Frankton Road.† A narrow zone of quartzose rocks exceedingly rich in stilpnomelane is associated with a thick lens of albite-epidote-chlorite schists three-quarters of a mile from Queenstown Post Office along the road to Frankton. The stilpnomelane schists at this new locality are similar to those described earlier (Hutton, 1938, pp. 178–179) that outcrop some 300–400 yards further to the east.

Stilpnomelane makes up about 90% of the particular schist from which that mineral was separated for analysis, and quartz, very minute euhedra of manganiferous garnet, usually segregated into dense semi-translucent laminae, clusters of large xenoblastic crystals of hydroxy-apatite, sphene, and yellow ferruginous epidote complete the mineralogical assemblage. However, among the thirty specimens examined the ratios of stilpnomelane to quartz show a wide range with as little as 20%

† Lake Wakatipu, Western Otago, New Zealand.

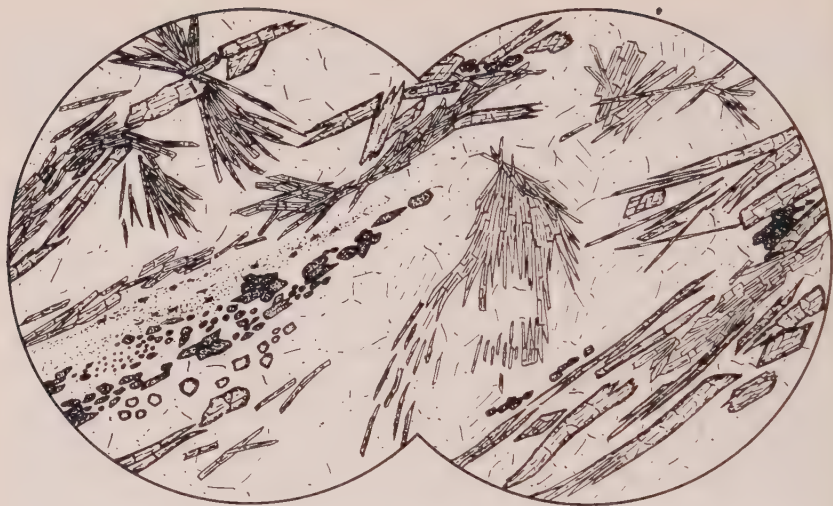


FIG. 1. Sheaf-like aggregates of stilpnomelane lie within or across the planes of schistosity in glaucophane schist. Albite, glaucophane, sphene, garnet, and quartz are associated minerals. San Juan Bautista Mine, near San Jose, California. Magnification $\times 11$.

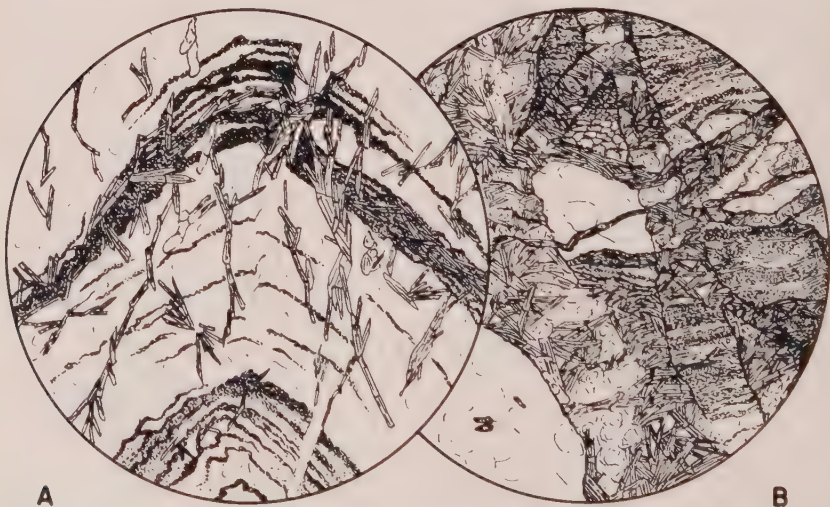


FIG. 2A. Crystallization of coarse plates of stilpnomelane has been guided to some extent either by tension during the very last phase of development of micro-folds, or by tension cracks that resulted from earlier flexure. Frankton Road, three-quarters of a mile from Queenstown Post Office, Lake Wakatipu, Western Otago, New Zealand. Magnification $\times 11$.

FIG. 2B. Late veinlets composed almost exclusively of stilpnomelane in quartz-garnet schist. Locality as for Fig. 2A. Magnification $\times 11$. Res. Coll. No. 21924.

of the former mineral in one instance. Albite was not observed in any specimen.

Stilpnomelane forms radiating sheaf-like aggregates and anastomosing networks of platelets (Fig. 2 *A* and *B*) that average about 0.2–0.3 mm. in length although a considerably coarser grain size is apparent in those schists in which stilpnomelane is less dominant—the more quartzose types. These rocks have undergone a considerable amount of deformation that would seem to have been largely, if not entirely, completed before crystallization of the bulk of the stilpnomelane occurred. Accordingly undeformed platelets and plumose aggregates are found in veinlets and tension cracks that cut across micro-folds and schistosity, and are also found to penetrate both post-deformation quartz veining and adjacent schist without interruption (Fig. 2 *A*). There appears to be little doubt that at least the major portion of the stilpnomelane crystallized after all movement had ceased.

TABLE 1. ANALYSES OF STILPNOMELANE

	<i>A</i>	<i>B</i>	<i>C</i>
SiO ₂	44.51	44.89	45.24
Al ₂ O ₃	7.20	6.98	5.27
TiO ₂	0.19	0.15	0.15
Fe ₂ O ₃	19.42	28.80	26.87
FeO	8.92	1.02	2.96
MnO	2.93	2.74	2.74
MgO	6.24	5.23	5.97
CaO	0.47	0.65	0.85
K ₂ O	0.86	1.30	0.57
Na ₂ O	0.37	0.42	0.75
H ₂ O ⁺	6.92	6.59	7.11
H ₂ O ⁻	-2.28	1.58	1.92
	100.33	100.35	100.40
α	1.584 \pm 0.003	1.620 \pm 0.003	1.605 \pm 0.003
γ	1.661	1.718	1.691–1.696
			1.694 for majority
γ - α	0.077	0.098	0.089
X	golden yellow	golden yellow	golden yellow
Y=Z	deep brown	deep red-brown	deep red-brown
S.G.	2.80 \pm 0.02	2.85 \pm 0.02	2.78 \pm 0.02

Analyses *A* and *B*: San Juan Bautista Mine, 3–4 miles south-east of San Jose, Santa Clara County, California. Analyst: C. Osborne Hutton.

Analysis *C*: Frankton Road, three-quarters of a mile from Queenstown Post Office, Western Otago, New Zealand. Analyst: R. Klemens.

MINERALOGY

The stilpnomelanes were prepared for analysis by the methods used in an earlier study (Hutton, 1938, p. 183) and preliminary fractionation was greatly facilitated by the highly brittle character of the minerals concerned since this allowed preferential reduction in grain-size with consequent concentration of the mineral concerned. The final pure fractions were secured by repeatedly centrifuging the nearly pure powders after they had been reduced in grain-size by careful grinding under acetone.

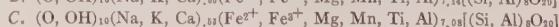
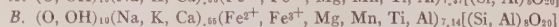
In the case of the Otago stilpnomelane a specific gravity of 2.78 ± 0.02 was found, but for the San Juan Bautista mineral, where a range of composition was evident from optical study alone, fractionation was found to be continuous over a density range of 2.79–2.86. Accordingly two fractions were separated in the latter instance, *viz.* one at 2.80 and a second at 2.85, but insufficient material of intermediate densities was obtained for analysis.

These analyses with their physical data are set out in Table 1. It will be noted that analyses *A* and *B* are similar except for the degree of oxidation of iron, and slightly lower magnesia and water content in the more highly oxidized mineral; total iron in these two analyses, expressed as Fe_2O_3 , is 29.36% and 29.93%. The similarity of the composition of stilpnomelanes *A* and *B* suggests that the change in ratio between Fe^{2+} and Fe^{3+} might be attributed to a very slow increase in pH of pore solutions (or oxidation potential) during crystallization of stilpnomelane

TABLE 2. STILPNOMELANE ANALYSES CALCULATED ON THE BASIS OF 30(O, OH) ATOMS TO THE UNIT CELL

	A Metals					B Metals					C Metals				
SiO ₂	44.51	7.92	} 0.08	8.00		44.89	7.93	} 0.07	8.00		SiO ₂	45.24	7.99	} 0.01	8.00
Al ₂ O ₃	7.20	1.41				6.98	1.45				Al ₂ O ₃	5.27	1.09		
			} 1.33					} 1.38					} 1.08		
TiO ₂	0.19	.02				0.15	.02				TiO ₂	0.15			
Fe ₂ O ₃	19.42	2.60	} 7.37			28.80	3.83	} 7.14			Fe ₂ O ₃	26.87	3.57	} 7.08	
FeO	8.94	1.33				1.02	.14				FeO	2.96	.43		
MnO	2.93	.44				2.74	.40				MnO	2.74	.41		
MgO	6.24	1.65				5.23	1.37				MgO	5.97	1.57		
CaO	0.47	.08	} 0.38			0.65	.12	} 0.55			CaO	0.85	.16	} 0.53	
K ₂ O	0.86	.18				1.30	.29				K ₂ O	0.57	.12		
Na ₂ O	0.37	.02				0.42	.14				Na ₂ O	0.75	.25		
H ₂ O	6.92	8.21				6.59	7.76				H ₂ O	7.11	8.37		

Formulae thus derived are:



rather than to weathering processes. In this connection it is possibly significant that the stilpnomelane with the higher percentage of Fe^{3+} also has a lower total water-content, and calculation of empirical cell

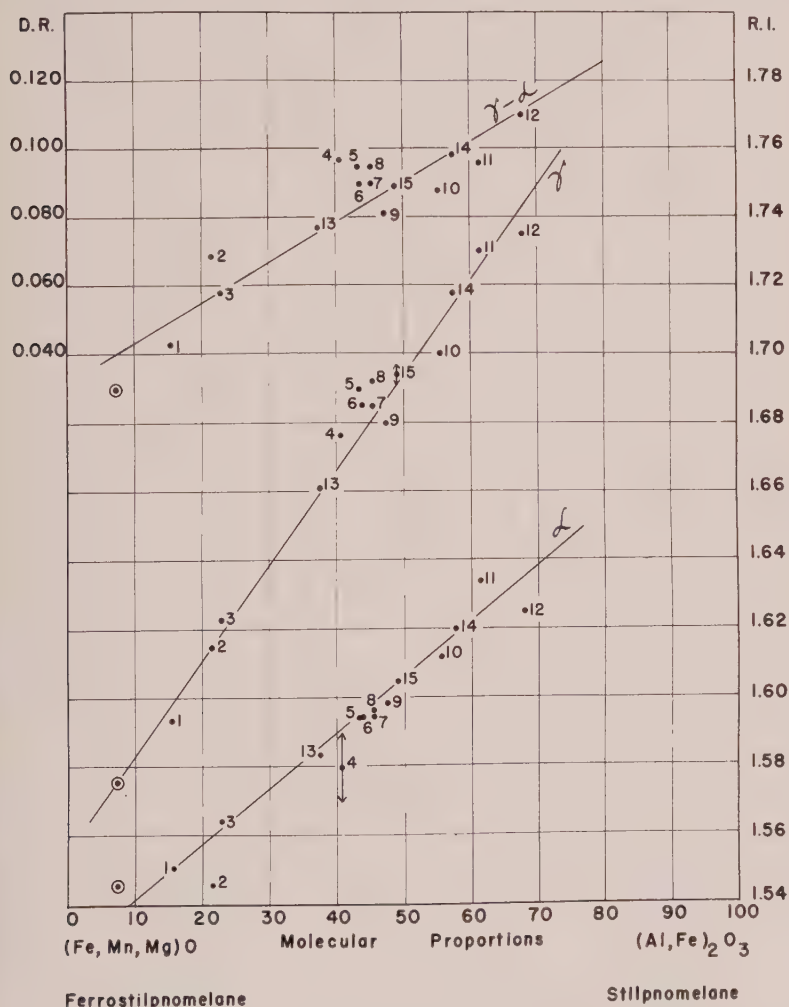


FIG. 3

- 1-12. These numbers correspond to those employed in Fig. 1 of Hutton (1945, p. 716).
 13. Less oxidized fraction, San Juan Bautista Mine, San Jose, California.
 14. Oxidized fraction, San Juan Bautista Mine, San Jose, California.
 15. Three-quarters of a mile along Frankton Road from Queenstown Post Office, Lake Wakatipu, Western Otago, New Zealand.
 Circled dot. Parsettensite (J. Jakob, 1923).

contents suggests that the lower water-content may be compensated for by increase in oxygen replacing hydroxyl.

The question of a formula for stilpnomelane cannot be satisfactorily settled until a structure analysis is made (Table 2). However, one can derive empirical cell contents if density and cell dimensions are known and at the same time make no assumptions as to the numbers of (O, OH) ions that might be present (Hey, 1954). Complete measurements of cell size have not been made by the writer for the three minerals described herein, although *c*-spacings were determined to be 12.14 Å., 12.10 Å., and 12.12 Å. for stilpnomelanes *A*, *B*, and *C* respectively. These data correspond closely with those secured by Gruner (1944, p. 294), *vis.* 12.07–12.18 Å. Thus for approximation purposes only it may be assumed that the stilpnomelanes described herein have comparable cell sizes to those already recorded by Gruner.

If we employ Gruner's cell volume and specific gravities of 2.80 and 2.82 for mineral *A* (Table 1) and a stilpnomelane previously studied (Hutton, 1945, p. 717, anal. 1) we arrive at cell weights of 1719.2 and 1731.5×10^{-24} gms., respectively. From these data an empirical oxygen content of 29.91 and 29.27 is obtained in each instance, figures that may be considered to have an accuracy of ± 0.75 , if a very generous margin for error in physical constants is allowed, since cell volumes have been used that have not been determined for material actually analyzed. No account is taken here of water given off below 105° C., but it is believed that a large part of this must be present as water molecules absorbed between the sheets. Certainly a previous experiment (Hutton, 1938, p. 191) clearly demonstrated that at least the greater portion of this water was not present as closely bonded hydroxyl ions.

Refractive indices have been plotted against the ratio (Fe, Mn, Mg)O : (Fe, Al)₂O₃ for fifteen analyses of members of the stilpnomelane group (Fig. 3), and the curves previously recorded by the writer (1945) are here slightly modified, and it is hoped, more correctly drawn.

The writer would like to acknowledge the opportunities for this research provided by a John Simon Guggenheim Memorial Fellowship.

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BRUSHITE AND TARANAKITE FROM PIG HOLE CAVE, GILES COUNTY, VIRGINIA

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ABSTRACT

Brushite occurs as nodular masses of platy crystals in the lower part of a bat guano and hair deposit in Pig Hole Cave, Giles County, Virginia. Taranakite occurs as flour-like masses near contacts between the guano and hair deposit and clay and along fractures within brecciated clay within the same cave. Chemical, physical, optical, x-ray, and thermal data for each of these minerals are presented. Some of the thermal data for brushite and many of the data for taranakite are reported here for the first time. It is suggested that the taranakite formed as the result of reactions between the bat guano and bat hair and clay.

INTRODUCTION

The presence of the minerals later identified as brushite and taranakite in a bat guano and hair deposit in Pig Hole Cave, Giles County, Virginia, was discovered in January, 1954. So far as has been ascertained by a search of the literature, this is the first reported natural occurrence of either brushite or taranakite in the United States of America. After positive identification of the minerals, further investigations of them were undertaken mainly because of their relative abundance within the cave.

LOCALITY AND OCCURRENCES

Pig Hole Cave is located beneath the property of A. B. Porterfield on Johns Creek Mountain in southeastern Giles County, southwestern Virginia. The cave was so named because of the former presence within it of the odoriferous remains of a pig lodged in a crawlway beneath the natural opening to the cave.

Pig Hole Cave has received special attention because of its proximity to Blacksburg, the home base of the VPI Cave Club, and because of the presence within the cave of relatively large deposits of bat guano. One natural entrance and one man-made entrance afford access. Entry through the natural entrance is gained by a drop of over 100 feet to the bottom of a sink hole; entry through the man-made entrance is gained by an eight-foot drop through a square tile to a crawlway that enters a room a short distance from the opening. The temperature of the air within the cave has been found to range between 8° C. and 10° C.

The cave is inhabited at the present time by a few "little brown bats" (*Myotis lucifugus lucifugus*) and possibly, as is suggested by fecal re-

mains, by a few other small mammals or possibly owls. Part of a jaw bone identified by H. S. Mosby of the VPI biology department to have belonged to an otter (*Lutra*) was found in the cave by W. D. Durham, Jr., in 1955. The bone may have been transported into the cave by some predatory animal; in any case, Professor Mosby notes that otters have been "extremely rare if present within the region for the last 50 or more years."

The cave is in a cherty limestone of mid-Ordovician age (B. N. Cooper, personal communication). Numerous fallen blocks (up to 15 feet in largest dimension), paucity of cave deposits, and numerous large rooms and deep wells characterize the cave. A few quartz crystals with curved faces occur attached to the roofs and walls of some passageways in the cave. Notable alluvial deposits constituted of cobbles and boulders of sandstone and quartzite plus silt and clay also occur within the cave. Clusters of transparent gypsum (selenite) crystals occur in the clay of the deposits in a few places; apparently they grew in place. Locally, the alluvial deposits are brecciated, probably as the result of desiccation. Taranakite occurs sporadically between some adjacent fragments of these "breccias."

A pit approximately five feet long, three feet wide, and five and a half feet deep is located about 75 feet from the man-made entrance to the cave. It was dug to investigate the size of the guano deposit in one of the rooms. It was in this pit that the brushite and taranakite were found first. The deposit, as exposed in the pit, has the following section: the upper foot is composed of a felt of brown hair (of bats) interlayered with nearly white excreta (now mostly gypsum); this admixture grades into a laminated white to buff colored zone, also composed of gypsum; the material of the bottom foot is distinctly different from that above—it is brown, generally massive, and contains masses of black carbonaceous material, brushite, and taranakite. The brushite occurs as nodular masses of minute crystals sporadically throughout this lower zone and the taranakite occurs as masses of a flour-like powder restricted to an even narrower zone adjacent to the clay bottom. The taranakite decreases in abundance upward away from the clay. The clay that forms the bottom of the pit is not unlike that of some of the alluvial deposits in the cave. A three to six inches thick zone of black carbonaceous material with small amounts of included gypsum is present between the guano and the limestone of the cave walls.

PREVIOUS WORK

Brushite and taranakite are both treated in the recent edition of Dana's System of Mineralogy (8). A few short papers dealing at least in

part with the minerals have appeared in the literature since this publication. Some of these papers are referred to directly below. Therefore, it is considered superfluous to include a summary of the literature here.

DESCRIPTIONS

Brushite.—The following properties were determined for the brushite from Pig Hole Cave.

Crystal System: Monoclinic

Physical Properties:

Thin plates. Perfect micaceous cleavage.

H.— $2\frac{1}{2}$. G. 2.30. Luster—vitreous.

Color—ivory yellow (Ridgeway color standard).

Transparent to translucent.

Optical Properties:

Colorless in transmitted light

Indices of Refraction $-\alpha = 1.54$

$\beta = 1.544$ (Calc.

from values of α , γ , and $2V$ by Mertie method)

$\gamma = 1.552$

Biaxial (+)

$2V = 59$ to 65°

$r < v$, inclined dispersion

Parallel extinction on laths and upturned edges of plates.

Chemical analysis:

Formula $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$		Theoretical Composition
CaO	31.9	32.6
P_2O_5	40.5	41.2
H_2O	27.5	26.2
	—	—
	99.9	100.0

Analyst: John Murray

Spectrographic analyses showed presence

also of Fe, Mg, Al, and Ni.

Solubility—0.0245 gm. of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ /100 gm. water at 25°C .

Thermal data¹: The heating curve for brushite is presented (Fig. 1). The information derived from x-ray examination of the products that exist after each reaction are noted below. These data corroborate the dehydration work of Sekanina (10) who showed that more than 20 per cent of H_2O is removed below 185°C . and that the remaining approximately 6.5 per cent H_2O is removed between 185°C . and 600°C .

Brushite exists until water is removed (indicated by the first endothermic reaction). Monelite, CaHPO_4 , then exists until the second reaction. The second endothermic peak apparently manifests the loss of hydrogen (as H_2O), in which case the final product is $\text{Ca}_2\text{P}_2\text{O}_7$. Neither

¹ Differential thermal equipment used—*FH305* furnace in vertical position heated at the rate of $12.5^\circ \text{C}/\text{min.}$; Leeds and Northrop x-y recorder; Pt+P+10 Rh thermocouple; three point system; scale multiplication of 10.

X-ray data:

X-ray setup—General Electric *XRD-3* diffraction unit with a No. 1 *SPG* geiger counter type spectrogoniometer; Cu $K\alpha$ radiation with Ni filter. Also, d values and relative intensities were corroborated with Co $K\alpha$ radiation with an Fe filter.

d , Å	I , approx. counts	d , Å	I , approx. counts
7.62	12,000	1.71	15
4.27	290	1.63	40
3.80	3,700	1.62	50
3.06	900	1.61	50
2.93	80	1.59	30
2.86	20	1.55	15
2.80	15	1.53	35
2.67	70	1.52	50
2.63	160	1.46	70
2.53	770	1.37	50
2.47	55	1.34	40
2.27	100	1.33	45
2.17	115	1.27	160
2.15	50	1.26	100
2.10	30	1.23	50
2.09	20	1.20	15
2.03	30	1.19	15
2.01	180	1.18	15
1.98	20	1.15	30
1.94	20	1.13	35
1.90	1,250	1.09	150
1.86	90	1.08	100
1.82	60	1.06	15
1.80	40	1.057	20
1.78	55	1.05	15

(94 degrees 2θ end of scan)

of these reactions showed reversibility in cooling curves. *X-ray* data for product B_3 are given below because they do not agree with data given for any previously reported calcium pyrophosphate.

PRODUCT B_3

d , Å	I , approx. counts
3.35	25
3.07	55
2.93 (d)*	50
2.71	10
2.41	10
2.23	20
2.22	15
2.10	10

* "(d)" signifies doublet.

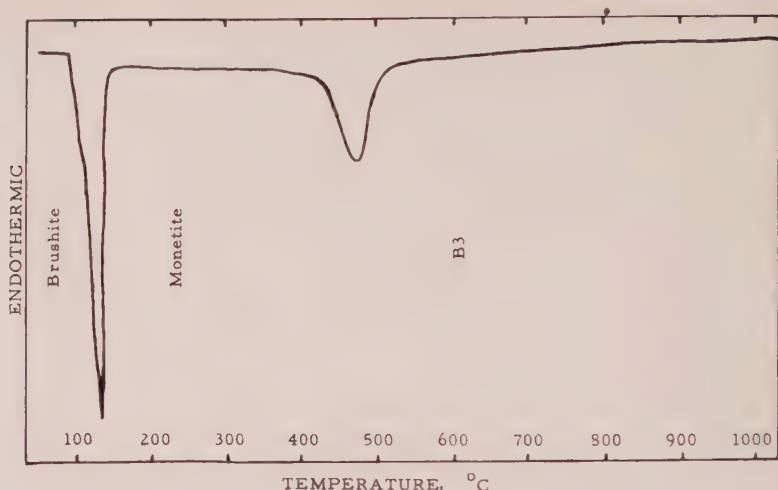


FIG. 1. Tracing of thermal (D.T.A.) curve of brushite.

Taranakite.—Except where noted otherwise, the following properties were determined for the taranakite from Pig Hole Cave.

Crystal system: Hexagonal (?)—on basis of optical uniaxiality and hexagonal shapes shown in photo-electronmicrographs by Haseman, *et al.* and Kittrick and Jackson (7). This does not agree with the “monoclinic . . . pseudo-hexagonal” reported by Haseman, *et al.* (5). However, Lehr (personal communication, 1955) states that “. . . we have extended the study on taranakite well beyond that reported in the paper of Haseman, Lehr, and Smith . . . a single-crystal Weissenberg study revealed that the unit cell is rhombohedral . . . we originally indexed taranakite as a monoclinic cell which is now shown to be a sub-unit of the rhombohedral cell. We did not recognize the rhombohedral character because of the unusually long *c*-dimension and because the earlier crystal preparations were too small to give good interference figures . . .”; this agrees with the “hexagonal” suggested here.

Physical Properties:

Massive, flour-like powder.

Color—white.

H.—soft G. 2.12. Insoluble.

Optical Properties:

Colorless in transmitted light

Indices of refraction: $\omega = 1.506$ – 1.510

$\epsilon = 1.500$ – 1.503

Birefringence: 0.006 – 0.007

Uniaxial (—)

Parallel extinction of laths.

(The values given for the indices of refraction are for the taranakite from the breccia and the taranakite from the pit, respectfully. Perhaps it is significant that the latter, which has the higher indices, has the higher $(\text{NH}_4)_2\text{O}$, Fe_2O_3 and H_2O contents.)

Chemical Analysis: The formula corresponding to the analysis of the taranakite from the brecciated clay is $3(\text{K}, \text{Na}, \text{NH}_4, \text{Ca})_2\text{O} \cdot 5(\text{Al}, \text{Fe})_2\text{O}_3 \cdot 7\text{P}_2\text{O}_5 \cdot 43\text{H}_2\text{O}$. It is apparent

that the bases present are insufficient to form normal phosphates. This is in agreement with the findings of Gautier (3). The formula given in the recent edition of Dana's System of Mineralogy (8) shows a basic phosphate although no analyses reported as yet show a high enough proportion of bases to support such a formula. Haseman *et al.* (5) state that they believe that the composition for taranakite is $2K_2O \cdot 3Al_2O_3 \cdot 5P_2O_5 \cdot 26H_2O$ and that deviations of natural taranakite from this may be referred to impurities. It appears that possibilities of substitution are numerous and that this fact has been overlooked by most previous workers.

Taranakite from pit Taranakite from breccia

K ₂ O	5.9	8.9
Na ₂ O	0.1	t
(NH ₄) ₂ O	1.8	0.8
CaO	0.6	0.4
Fe ₂ O ₃	1.7	0.8
Al ₂ O ₃	17.0	19.5
P ₂ O ₅	38.9	38.4
H ₂ O	34.9	30.3
Rem. (Insol.)	1.3	0.6
	102.2	99.7

Analyst: John Murray

Spectrographic analyses showed the presence also of Ag, Cu, Ga, Mn, Mg, Pb, Si, and Ni. X-ray data are presented at top of the next page. Thermal data:² The heating curve for taranakite is presented (Fig. 2).

Taranakite exists until part of its water is given off, the reaction that is manifest by the first endothermic peak; T_1 has an x-ray pattern similar to that of the lower hydrate as reported upon by Haseman *et al.* (5); after the next endothermic reaction, apparently dependent upon the loss of the remaining water, product T_2 is obtained—this product is amorphous to x-rays; the exothermic reaction appears to represent an irreversible (according to the cooling curve) reconstructive inversion of T_2 to product T_3 ; T_3 is changed to T_4 as the result of the endothermic reaction near the end of the heating curve. X-ray data obtained for T_3 and T_4 do not correlate with any published patterns. Perhaps, although chemical analyses of the product do not corroborate this, this last reaction represents a loss of part of the phosphorus. The position of the end of the curve may represent the beginning of another reaction or merely a difference in conductivity of material T_4 from that of T_3 .

GENESIS

It has been reported that brushite is "Widespread in small amounts in insular and continental phosphate deposits. [and] Frequently occurs

² Differential thermal analysis equipment used was the same as that used for the brushite.

X-ray data:

X-ray setup used was same as that for brushite. Further, diffraction patterns of taranakite from Pig Hole Cave and those of minervite from Cesse, Grotto De Minerva, France (U. S. National Museum specimen number *R5531*) as obtained by using a 114.6 mm. Philips camera and Cu K α radiation, were compared and found to be essentially equal.

d , Å	I , approx. counts	d , Å	I , approx. counts
15.49	3250	1.92	15
7.82	750	1.90	60
7.43	570	1.88	25
7.13	190	1.86	40
5.82	420	1.84	20
5.01	140	1.83	15
4.62	110	1.82	50
4.27	390	1.79	55
4.15	60	1.77	40
4.00	110	1.75	15
3.79	800	1.74	25
3.72	350	1.71	60
3.57	500	1.68	45
3.34	300	1.65	15
3.27	320	1.64	55
3.16	300	1.62	30
3.12	620	1.61	35
3.06	30	1.593	20
2.94	140	1.588	20
2.83	390	1.57	15
2.81	400	1.52	15
2.73	250	1.50	15
2.70	90	1.48	25
2.62	430	1.47	15
2.55	90	1.42	50
2.53	70	1.39	20
2.48	40	1.35	20
2.44	20	1.33	25
2.38	230	1.32	15
2.34	50	1.313	20
2.26	90	1.312	20
2.17	50	1.28	35
2.14	50	1.23	25
2.12	35	1.22	25
2.09	80	1.20	25
2.06	150	1.17	20
2.00	15	1.12	20
1.96	60	1.11	15

(88 degrees 2θ end of scan)

as an incrustation upon ancient human and animal bones and has been observed in human urinary calculi" (8). It might be suggested that the shapes of the masses of crystals in the guano pit at Pig Hole Cave

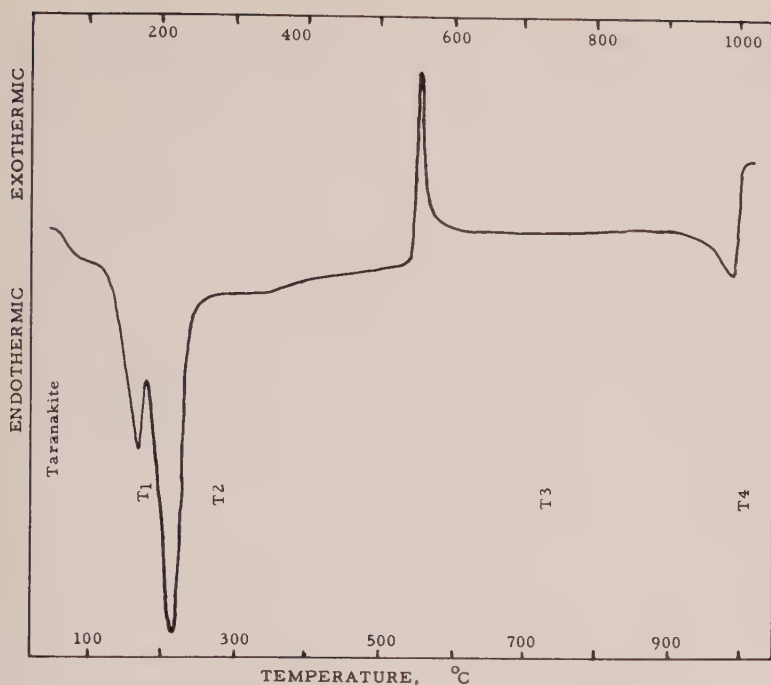


FIG. 2. Tracing of thermal (D.T.A.) curve of taranakite.

indicate that the brushite here represents former bones included in the deposit. Although this does not appear to be likely to the writers, it admittedly has not been possible to prove or disprove the possibility. That this occurrence is in a perennially damp location just as are most of the previously reported occurrences, appears to indicate this condition to be a major control. Other than this, only the possible role(s) of the decaying of the bat hair along with the decaying guano appears to offer anything new concerning the origin of brushite.

The occurrences of the taranakite in the brecciated clay and within the bat guano deposit in the zone adjacent to the bottom clay plus the composition of it and of each of these materials suggest that the taranakite was formed by interactions between the bat guano (and possibly the bat hair) and the clay. If this origin did obtain, at least most of the aluminum would have been derived from the clay and the potassium and phosphorus from the guano and/or hair. This appears to be possible considering the composition of clay minerals, of bat guano, and of bat hair.

This suggested origin appears to be corroborated by the work of Gautier (3) and by the recent investigations of numerous soil scientists,

for example, Haseman *et al.* (4) Gautier showed that in nitrogenous material of animal origin most of the phosphorus is retained as $(\text{NH}_4)_2\text{HPO}_4$ and that this can react with argillaceous or calcareous material to produce phosphates of aluminum or calcium. Haseman, *et al.* showed, that in conjunction with phosphate fixation by soil minerals (mainly clays) that aluminum phosphates are the end products of the phosphate-induced decomposition of kaolinite. Further, Kittrick and Jackson (7) reported that they were able, by using an electron microscope, to observe during the process the actual progressive formation of different aluminum phosphate crystals concomitantly with the decomposition of kaolinite crystals. It is perhaps of special interest that "Taranakite-like crystals" formed in one of their experiments (apparently the Na-analogue of taranakite according to the formula they give). As the result of their observations, these last two workers concluded that "It can be seen then that the formation of aluminum phosphates at the expense of kaolinite is a solution-precipitation phenomenon involving dissociation of aluminum from the kaolinite crystal, which is in accord with the aluminum-dissociation and solubility product principles advanced . . . to explain phosphate fixation by soil minerals."

Apparently the main control is that taranakite (and other minerals such as leucophosphite and minyulite) must form in the presence of an excess of the proper alkali ion otherwise the alkali will be lost and varisite (or related strengite or barrandite) will form (1, 5). A further control appears to be the constant or nearly constant presence of water (at least dampness)—Hutchinson (2) noted that the mineral has been found only in areas that are perennially damp; the Pig Hole Cave occurrence is no exception.

Because of the likelihood that at least most of the aluminum of the taranakite was derived from the clay, x-ray and differential thermal analyses were made of the brecciated clay associated with the taranakite in order to determine if the clay of the fragments showed evidences of any changes in composition near their contacts with the taranakite. Samples from the zones within approximately one millimeter of the contact (hereinafter referred to as "O" for outer) and samples from the part of the breccia fragments farthest from the taranakite (hereinafter referred to as "I" for inner) were analyzed. The analyses showed the O sample to have no kaolinite whereas the I sample does contain some; illite appears to be better crystallized in the I sample than in the O sample; quartz appears to make up a slightly greater percentage of sample O than of sample I; vermiculite(?) is present in only the O material; analyses of ethylene glycol-saturated samples of each material indicate that they both contain minor amounts of halloysite. These data suggest that under

the conditions prevalent at the locality when the taranakite was formed, *i.e.*, when there was a presence of phosphate solutions, that aluminum was more readily available from kaolinite than from illite. Apparently, while the illite started to break down, and in part perhaps did break down to vermiculite—thus arresting further release of aluminum, kaolinite broke down completely thus releasing its aluminum for formation of aluminum phosphates. There also is the possibility, however, that these processes did not occur as direct consequences of the special conditions set up in the cave but rather that they occurred because of more or less normal weathering in which case the above noted relationships might not pertain to the problem at all. This alternative is suggested by the recent findings of Rich and Obenshain (9, and Rich, personal communication) who have reported similar relationships to occur in a Virginia soil. They report that from the surface downward that kaolinite content increases, illite content (and degree of crystallization) increases, and dioctahedral vermiculite content decreases.

One other fact concerning taranakite warrants further investigation because of its possible relation to genesis of the mineral. Hutchinson (2) noted that in his spectrographic analysis of minervite that along with many other elements, Pb was present. He noted that the lead might be a contaminant. The spectrographic analyses made in conjunction with this investigation also showed, along with many other elements, Pb. In fact, Pb was the only element that occurred in the taranakite that was not found to occur in either the guano or the adjacent clay. There appears to be no way in which the taranakite collected and analyzed by the writers could have been contaminated. It therefore appears that an affinity must exist between lead and the taranakite lattice. Perhaps the correct answer is that suggested in a later publication by Hutchinson (6) *i.e.*, “. . . minute amounts of Pb^{++} ($r=1.32 \text{ \AA}$) may conceivably replace K^+ ($r=1.33 \text{ \AA}$) in the mineral.” It appears quite possible that such a substitution could occur in conjunction with one or more of the substitutions suggested as possible by the tentative formula for taranakite given here.

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This investigation was initiated by Murray at the suggestion of Professor Clifford Frondel as passed on to him by W. J. Foster.

Mr. A. B. Porterfield, owner of the land under which Pig Hole Cave is located, allowed the writers to enter the cave and collect minerals from it. C. I. Rich, Webster Richardson, and H. D. Ussery, who are, respectively, in charge of the Agronomy *x*-ray and differential thermal laboratory, the Physics department *x*-ray laboratory, and the Physics department spectrographic laboratory at Virginia Polytechnic Institute,

aided in their laboratories. J. J. Glass of the Geochemistry and Petrology Branch of the U. S. Geological Survey checked all of the optical data for brushite and some of the data for taranakite. George Switzer of the U. S. National Museum and B. W. Nelson of the Department of Geological Sciences at Virginia Polytechnic Institute critically read the manuscript. The writers gratefully acknowledge all these contributions.

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DETERMINATION OF RANDOM INTERSTRATIFICATION IN MONTMORILLONITE

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ABSTRACT

In the study of clay minerals, x -ray diffraction patterns are often obtained for samples which are not pure minerals but are mixtures in which layers of different types alternate. There are three types of interstratification: (1) random, (2) regular, (3) segregated into zones in the individual crystallites. The usual method of determining the degree and type of random interstratification is by the method of Hendricks and Teller by which theoretical scattering curves are constructed for the various mixtures. The method presented here is a Fourier transform method which can be used to calculate the degree and type of interstratification directly from the measured x -ray data.

Fourier transforms have been calculated for a series of sodium-calcium montmorillonites from 100% sodium and 0% calcium to 0% sodium and 100% calcium. Intensities of the various Fourier peaks give a good representation of the type of random interstratification in the samples. The intensities are also related to the amount of monovalent and divalent ions. Therefore, by using the experimental x -ray diffraction data alone, one can estimate the degree and type of random interstratification in montmorillonite.

INTRODUCTION

Very often in the study of clay minerals x -ray diffraction patterns are obtained for samples which are not pure minerals but are mixed structures in which layers of different types alternate. Naturally occurring clay minerals of this type have often been reported in the literature.¹

These mixed layer type clay minerals are easily formed in nature since most of the clays are layer structures and it is a simple matter for the different layers to alternate. There are three types of interstratification, namely (1) random, (2) regular, and (3) segregated into zones in the individual crystallites. One of the most usual ways in which random interstratification can occur is by the existence of two or more different degrees of hydration. Examples are mixed layers of mica with montmorillonite or vermiculite, glycerol saturated montmorillonites in which a certain proportion of layers of lower glycerol content is present, or two or more successive hydrates of montmorillonite.

It has been shown^{2,3} that ideally at room temperature the sodium montmorillonite would have a "single water layer" resulting in a (001) spacing of 12.4 Å, while calcium montmorillonite would have a "double water layer" and corresponding (001) value of 15.4 Å. Randomly interstratified

¹ Brindley, G. W. (Ed.): *X-ray identification and crystal structure of clay minerals: The Mineralogical Society, London (1951).*

² Roth, R. S., Ph.D. Thesis, University of Illinois, Urbana, Illinois (1951).

³ Williams, F. J., Nezayko, M., Weintritt, D. J.: *J. Phys., Chem.*, **57**, 6 (1953).

mixtures of these two types of hydration would lead to intermediate (001) values and non-integral higher orders.

Hendricks and Teller⁴ have calculated the scattering which would be given by random and partly random mixtures. By use of these formulae, it is possible to construct curves showing the type of scattering to be expected from various mixtures.⁵ However, since this method can require the calculation of a very large number of curves it has been found desirable to have a direct method of getting the required information from the measured x -ray data.

Mering⁶ has pointed out that the Fourier transform of the diffraction diagram can be utilized to obtain the needed information on interstratification. MacEwan⁷ has applied a Fourier transform technique to theoretical random mixtures of 10 and 12 Å spacings with mica-type layers. These results indicated the usefulness of this method.

The purpose of this investigation was to apply the method of Fourier transforms to analyze random interstratification mixtures of sodium and calcium montmorillonites. By using the experimental diffraction data alone it is possible to estimate the degree and type of interstratification in this system.

MATERIALS AND EXPERIMENTAL METHODS

The purified bentonite samples employed were prepared by the method described by Williams, Neznayko, and Weintritt.³ The preparation of samples for x -ray examination involved a procedure which would yield diffraction data of only the basal spacings. A dilute, fully hydrated suspension of the clay was allowed to slowly air dry on a glass microscope slide. The air dried sample was then placed in a desiccator maintained at a relative humidity of 52%, and allowed to come to equilibrium. These oriented samples were then run on a North American Philips High Angle Spectrometer using Ni filtered Cu K α x -radiation. The relative humidity of the room in which the x -ray diffraction was carried out was maintained at approximately 50%, so that there was no change in the spacings during the x -ray examination.

EXPERIMENTAL RESULTS AND DISCUSSION

The Fourier transformation which was employed in these calculations was that published by MacEwan.⁷ The cosine transform

$$T(R) = \int_0^\infty \frac{I(\mu)}{\Theta |F_l|^2} \cos 2\pi\mu R d\mu$$

⁴ Hendricks, S. B., and Teller, E.: *J. Chem. Phys.*, **10**, 47 (1942).

⁵ Brown, G., and MacEwan, D. M. C.: *J. Soil Sci.*, **1**, 239 (1949).

⁶ Mering, J., *Acta Cryst.*, **2**, 371 (1949).

⁷ MacEwan, D. M. C.: *Nature*, **171**, 616 (1953).

TABLE 1. X-RAY DIFFRACTION BASAL SPACINGS AND RELATIVE INTENSITIES OF SODIUM-CALCIUM MONTMORILLONITES

Sample	1st Order	2nd Order	3rd Order	4th Order	5th Order
	$d(\text{\AA})$ I/I_0	$d(\text{\AA})$ I/I_0	$d(\text{\AA})$ I/I_0	$d(\text{\AA})$ I/I_0	$d(\text{\AA})$ I/I_0
100% Na- 0% Ca	12.6 100	6.23 8.9	4.25 0.2	3.12 32.0	
80% Na- 20% Ca	12.6 100	6.23 8.8	4.20 0.2	3.10 38.6	
60% Na- 40% Ca	14.0 100	6.22 0.6	5.18 0.5	4.01 0.3	3.09 35.0
40% Na- 60% Ca	14.7 100		5.13 0.6	4.03 0.3	3.07 23.8
20% Na- 80% Ca	14.9 100		5.04 9.4	3.78 0.1	3.02 17.4
0% Na-100% Ca	15.1 100		5.03 12.1	3.75 0.2	3.01 13.4

is essentially the Patterson line projection on the c -axis of the crystallites. Its values are proportional to the mean number of layers at a distance R from any arbitrary layer chosen as the origin. This form of function gives a peak at the origin and the terms are as follows: $I(\mu)$ is the observed intensity for each value of the reciprocal spacing, F_l is the structure factor of a single layer and Θ is the Lorentz-polarization factor.

The above transform may be approximated by the following summation:

$$T(R) \approx \sum_R \frac{I_R}{\Theta |F_l|^2} \cos 2\pi\mu_R R$$

This sum makes use of the observable data and has the number of terms equal to the number of lines. The technique employed in obtaining the x-ray diffraction data leads only to basal reflections, consequently all the diffraction peaks observable were employed in the calculations. Table 1 gives the x-ray diffraction and relative intensity data of the series of purified montmorillonites.

Since there were only a few basal lines observed the high order terms were artificially diminished by application of an artificial temperature factor, $\exp(-A \sin^2 \theta)$ where A has a value of 25. This value of A was chosen so as to reduce the value of the exponential to about 0.10 at a value of $\sin \theta/\lambda = 0.25$, which corresponds to the smallest observed spacing in this series of clays.

The calculated transforms are shown in Fig. 1. It will be noted that good separation of the 12.4 and 15.4 \AA spacings is obtained. The relative intensities of the various peaks are shown in Table 2, the most intense peak having a value of 100 arbitrary units. Peaks of the single water layer or sodium type have been designated as A , while the double water layer or calcium type is labeled B . The combination peaks such as AB arise from two units of the 12.4 \AA type and one of the 15.4 \AA type in any order. The relative intensities of the combination peaks approximate the randomness of the mixture.

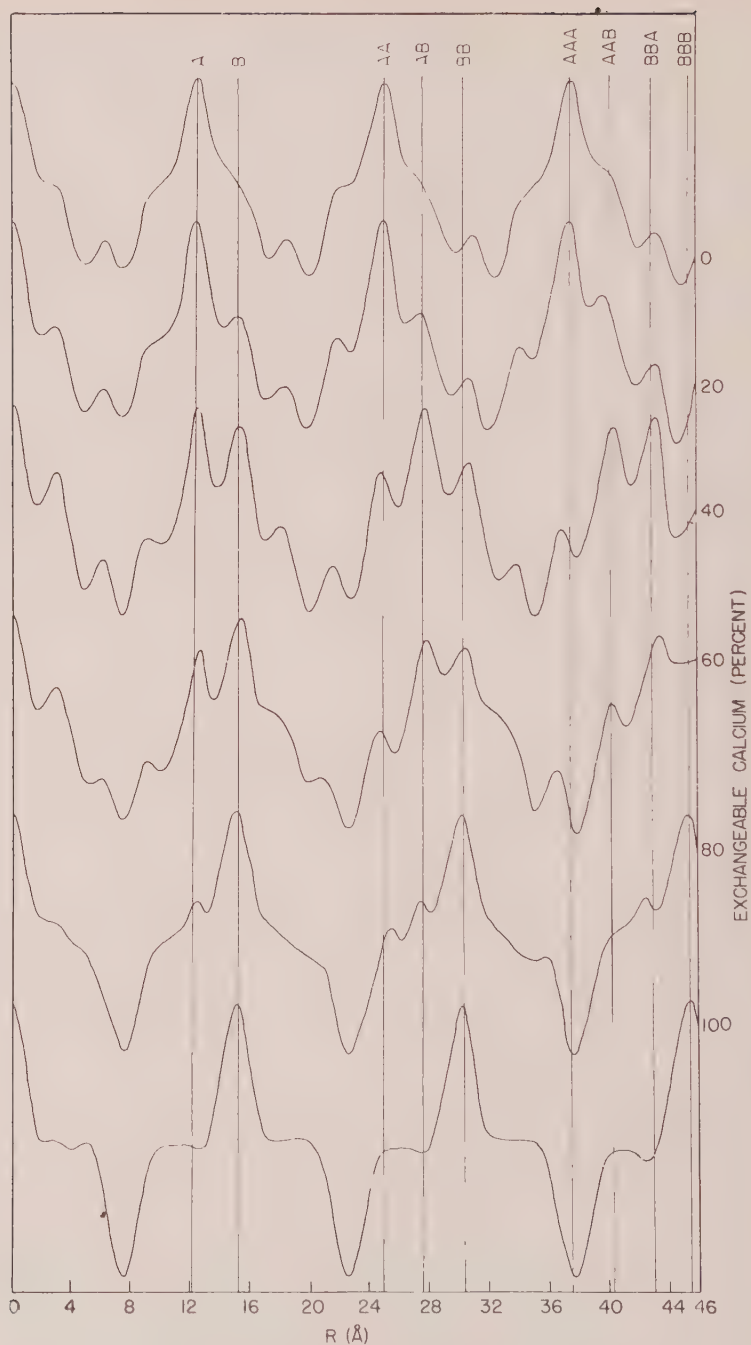


FIG. 1. Fourier transforms of sodium-calcium montmorillonites.

TABLE 2. RELATIVE INTENSITIES OF THE CALCULATED FOURIER PEAKS OF SODIUM-CALCIUM MONTMORILLONITES

Sample	Relative Intensities of Fourier Peaks								
	A 12.5 Å	B 15.2 Å	AA 25.0 Å	AB 27.7 Å	BB 30.4 Å	AAA 37.5 Å	AAB 40.2 Å	BBA 42.6 Å	BBB 45.6 Å
100% Na- 0% Ca	100		100			100			
80% Na- 20% Ca	100	20	100	25		100	30		
60% Na- 40% Ca	100	75	35	100	50		70	80	
40% Na- 60% Ca	70	100		80	70		20	80	55
20% Na- 80% Ca	20	100		25	100			30	100
0% Na-100% Ca		100			100				100

The transforms of the 100% sodium and 100% calcium montmorillonites show only the peaks related to the 12.4 Å and 15.4 Å lines, respectively. The transform of the 80% sodium, 20% calcium sample shows that there is a relatively large amount of material of the *AB* type and *AAB* type.

The relative intensities of the peaks of the 60% sodium, 40% calcium sample show a very large amount of the *AB* type, in fact much more than either the *AA* or *BB* types. There is also a considerable amount of *AAB* and *BBA* material as represented by the peaks at 40.2 and 42.6 Å. These results would indicate that for the most part this sample is made up of alternating layers of *A* and *B*, with lesser amounts of other combinations. It will be noted that for the 40% sodium, 60% calcium samples there are about equal amounts of *AB* and *BB* type material. This is a somewhat different distribution than observed for the preceding sample. In the 20% sodium, 80% calcium sample it is shown that a large amount of the *A* type material is combined with *B* as *AB* or *BBA*.

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VARIATIONS IN X-RAY POWDER DIFFRACTION PATTERNS OF PLAGIOCLASE FELDSPARS

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ABSTRACT

The angular separation between the $(\bar{1}\bar{1}1)$ and (131) reflections in x-ray diffractometer patterns of 66 chemically analyzed natural plagioclases, 11 plagioclases synthesized in the dry way, and 4 plagioclases synthesized hydrothermally has been measured and plotted against composition. By this criterion, plagioclases synthesized in the dry way and natural plagioclases from thick stratiform mafic intrusions constitute two distinctly different series, each of which is closely defined by a single curve. Natural plagioclases from volcanic and hypabyssal rocks and plagioclases synthesized hydrothermally are intermediate between the two series. Other natural plagioclases, some of which have been assumed by others to belong to a "low-temperature" series, do not belong to either of the series mentioned above, and cannot be represented by any single curve. It is concluded that composition determinations cannot be made by the use of the available curves based on the variation of reflection separations, because there is no a priori way of knowing how closely a given plagioclase is represented by a particular curve. However, given the composition of a plagioclase, the curves are useful for making an estimate of its degree of inversion toward some undefined low-temperature state.

INTRODUCTION

Certain parameters in the atomic structures of plagioclase feldspars vary with composition and with thermal history. The variations may be studied by measuring the angular separation of two reflections in x-ray powder diffraction patterns, a procedure which avoids some of the errors encountered in measuring the absolute positions of the reflections. Previous workers have published the results of several such studies. Claisse (1950) studied eight samples of plagioclase, disregarding the thermal histories of the samples. Tuttle and Bowen (1950) and Chayes and Robbins (1953) studied samples covering limited parts of the composition range. In a more extensive study, Goodyear and Duffin (1954) presented curves showing the variation of reflection separations with composition in synthetic plagioclases and in natural plagioclases; they also studied the effects of heating natural plagioclases (1955). J. V. Smith (1956) has carried out a detailed study of the variation of lattice parameters and reflection separations in synthetic and natural sodic plagioclases.

The present writers planned to use the x-ray methods recommended by Goodyear and Duffin to determine the composition and thermal state of plagioclases synthesized in experimental studies of the system albite-anorthite-water. In order to check the reproducibility of Goodyear and Duffin's results with different equipment, reflection separations in several

chemically analyzed samples of natural plagioclases were first measured and compared with Goodyear and Duffin's curves. Significant discrepancies suggested that the 16 samples of natural plagioclases studied by Goodyear and Duffin are not representative of *all* so-called low-temperature plagioclases. In order to investigate more fully the nature of the variations to be expected in x-ray parameters of plagioclases, 66 chemically analyzed samples of natural plagioclases, 11 synthetic plagioclases crystallized in the dry way, and 4 synthetic plagioclases crystallized hydrothermally were studied.

EXPERIMENTAL METHODS

The reflections to be measured were chosen on the basis of the following requirements: (*a*) that they be clearly resolved from neighboring reflections, (*b*) that their 2θ values vary sensitively with composition, and (*c*) that two such reflections, between which the angular separation is to be measured, be close together in powder patterns to minimize chart-scale errors. A pair of reflections which satisfies these requirements over the composition ranges An 0 to An 30 and An 60 to An 100* in natural plagioclases is (131) and (131).† A second pair, (220) and ($\bar{1}\bar{3}1$), is equally suitable over the composition ranges An 10 to An 30 and An 60 to An 100, but the (220) reflection crosses the ($\bar{2}\bar{2}0$) reflection at An 10 and is masked by strong (040) and (002) reflections from An 0 to An 10.‡ The (220), (131), and ($\bar{1}\bar{3}1$) reflections are resolved in plagioclases synthesized in the dry way from An 0 to An 100. Appropriate portions of powder patterns of high-temperature albite and of natural albite, andesine, and anorthite are shown in Fig. 1. The relevant data on the reflections are given in Table 1.

Specimens were prepared by smearing suspensions of powder in lacquer-acetone solution on glass slides. Powder patterns were taken with a

* Unless otherwise stated, compositions are given as

$$\text{mol \% } \frac{\text{An}}{\text{An} + \text{Ab} + \text{Or}}$$

throughout this report.

† Powder patterns were indexed by comparison with completely indexed patterns of Amelia albite in the natural state and in a high-temperature state (heated at near-melting temperature until no further change took place in the lattice parameters of the quenched product). J. V. Smith (1956) indexed the patterns of Amelia albite, and kindly made the information available to the writers.

‡ This fact is not taken into account by Goodyear and Duffin (1954), who, by measuring the (220)–($\bar{1}\bar{3}1$) separation for pure albite and including it with measurements of the non-equivalent (220)–($\bar{1}\bar{3}1$) separation for more calcic plagioclases, have introduced considerable error (4 to 7% An) in their *A-B* curve for low-temperature plagioclases in the range An 0 to An 30.

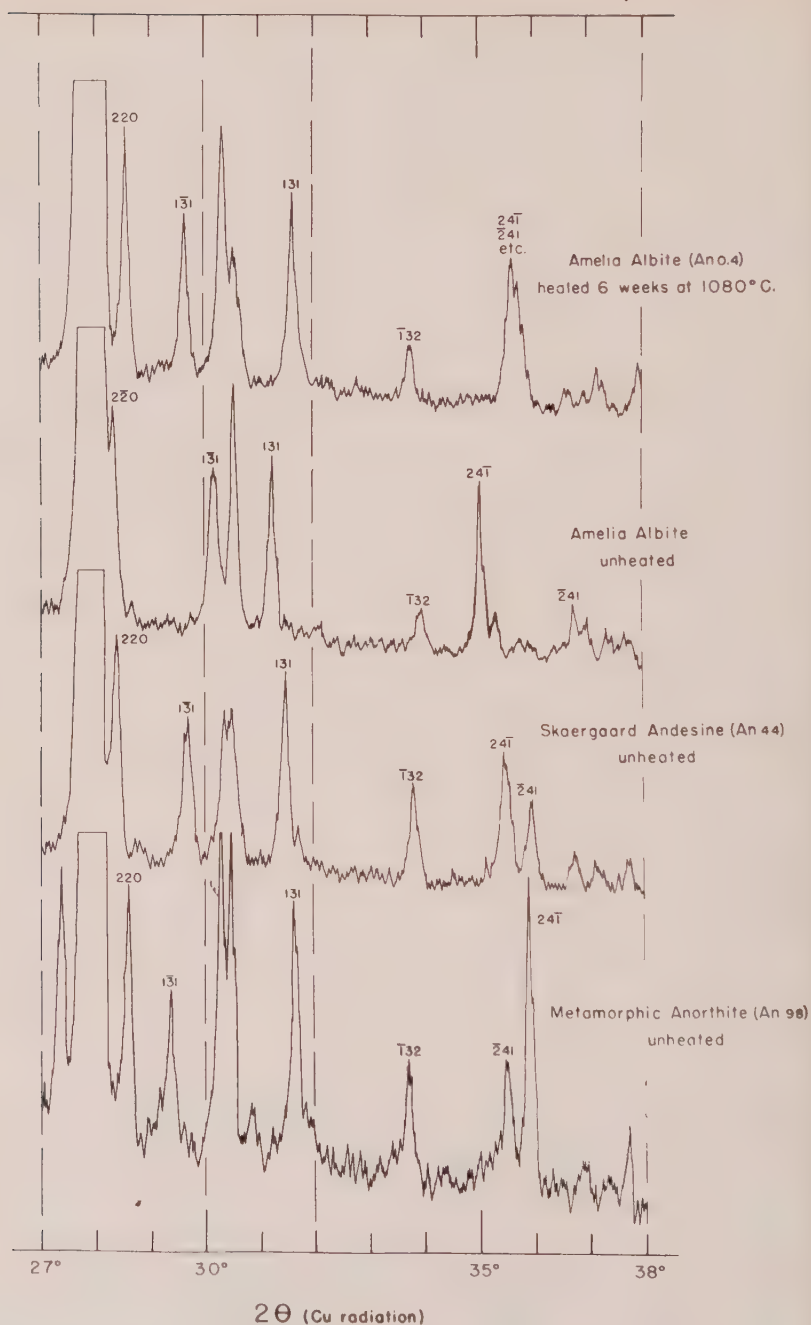


FIG. 1. Portions of powder diffraction patterns of Amelia albite changed by heating to the high-temperature form, and of unheated natural albite, andesine, and anorthite.

TABLE 1. POSITION OF SIGNIFICANT REFLECTIONS

Indices	2θ (CuKα)			Remarks
	Low-temp.	High-temp.	An	
	Ab	Ab		
(220)	28.1 (calc.)	28.5	28.6	Crosses (220) at approximately An 10 in low-temperature plagioclases
(131)	30.1	29.6	29.4	May or may not be resolved in inhomogeneous low-temperature plagioclases in the range An 6 to An 17
(131)	31.2	31.6	31.6	Resolved from An 0 to An 100

Norelco high-angle diffractometer using copper K α radiation. Divergent and scatter slits were 1° , receiving slit 0.006 inch, scan speed $\frac{1}{4}^\circ$ per minute, and chart scale 2 inches per degree. The appropriate 2θ region was scanned at least three times; the reflection separations were measured to the nearest $0.01^\circ 2\theta$, and the measurements were averaged arithmetically.

Table 2 is a list of the samples and the measurements obtained from each. In the samples of natural plagioclases, the maximum range of the individual measurements of the reflection separations in one sample is 0.10° , and in most of the samples the range is 0.04° or less. Taking into account the variable quality of the peaks in the powder patterns, the probable accuracy of the average value of a reflection separation for any sample of natural plagioclase is estimated to be $\pm 0.02^\circ 2\theta$ or better. The accuracy for the sodic and intermediate synthetic plagioclases is somewhat less than this, owing to the broad character of the peaks. In the plots of the data (Figs. 2, 3, and 4) the size of the symbols has been made $0.04^\circ 2\theta$, which approximately covers the range of uncertainty of the position of each point in the direction of the reflection separation axis. The uncertainty to attach to the positions of the symbols in the direction of the composition axis cannot be estimated quantitatively on the basis of the chemical analyses themselves, but it is believed to be no greater than ± 2 mol % An for most of the samples. Like most natural plagioclases, the samples used have varying amounts of K $_2$ O (see Table 2). The amounts represent less than 4.5 mol % Or in any sample other than the Larsen samples from volcanic rocks and Howie's sample 2270 from a charnockite, in which samples the maximum content of Or is 10.5 mol %. The effect on x-ray parameters of plagioclases of K $^+$ ions present in the structure is not known. Especially in the samples with

high K_2O contents, an undetermined part of the K_2O is probably present in a separate phase, which would contribute small errors to the calculated compositions of the samples.

DISCUSSION OF RESULTS

In Fig. 2 the $(\bar{1}\bar{3}1)-(131)$ separation is plotted against the known compositions of 11 plagioclases synthesized in the dry way (circles) and 11 plagioclases from thick stratiform mafic intrusions (squares). With one exception, the points representing the synthetic plagioclases fall, within the limits of error, on the curve drawn through them. The curve represents plagioclases crystallized at and cooled quickly from temperatures slightly below the solidus for the dry system $Ab-An$.*

The points representing plagioclases from thick stratiform mafic intrusions—namely, the Skaergaard intrusion, the Great Dyke, the Bushveld igneous complex, and the Stillwater igneous complex—fall on the curve drawn through them within the limits of error. *All these plagioclases probably have similar thermal histories*, inasmuch as they all crystallized at basaltic magma temperatures, and, as a result of the tremendous thickness of the intrusions, cooled very slowly during and after crystallization. In view of their lower temperatures of crystallization and much slower rates of cooling as compared with the plagioclases synthesized in the dry way, it may be assumed that the plagioclases from thick stratiform mafic intrusions are modifications which are either in equilibrium at temperatures lower than the temperatures from which the plagioclases synthesized in the dry way were quenched, or are transitional toward some lower temperature equilibrium state. Since these plagioclases are the most slowly cooled of all magmatic plagioclases in the composition range which they cover ($An\ 36$ to $An\ 86$), and since they make up a well-defined series by the criterion of reflection separations, they will be called “plagioclases of the Bushveld type” in this report. This is in accordance with Hess’s (1952) designation of orthopyroxenes

* The curve does not represent plagioclases at near-solidus temperatures, because MacKenzie (1952) has shown that there are marked differences between reflection separations in synthetic sodic plagioclases at room temperature and at elevated temperatures, and that the reflection separations change on cooling to room temperature, no matter how rapid the cooling rate. Goodyear and Duffin cite discontinuities in the variation of reflection separations measured at room temperature for synthetic plagioclases as evidence of lack of complete solid solution in high-temperature plagioclases, “although the early work of Bowen (1913) on melting phenomena indicated solid solution over the whole range from albite to anorthite” (Goodyear and Duffin, 1954, p. 321). Bowen’s data concern equilibrium conditions at the solidus temperatures. From MacKenzie’s work, it is evident that discontinuities in the variations of x-ray parameters measured at room temperature may have no bearing on whether or not complete solid solution exists at solidus temperatures.

TABLE 2. LIST OF SAMPLES AND DATA

(continued)

(continued)

TABLE 3. CHEMICAL ANALYSIS OF BYTOWNITE HGIF-AN-53

	Wt. %	Mol numbers	
SiO ₂	44.87	747	
Al ₂ O ₃	34.93	342	
TiO ₂	0.01		Mol % An*
Fe ₂ O ₃	0.09		$= \frac{311+7}{(311+7)+2(16+4.5)} \times 100$
FeO			
MgO			
SrO	0.00	7	= 88.7
CaO	17.41	311	
BaO	0.00		
Na ₂ O	0.98	16	
K ₂ O	0.42	4.5	
Rb ₂ O	0.00		
H ₂ O+	0.59		
H ₂ O-	0.04		
	100.04		

Analyst: Eileen H. Oslund.

Collector: Allan H. Nicol.

Occurrence and locality: Large single crystal in vein-like mass in hornblende-actinolite schist, Olricksfjord area, N. W. Greenland.

Alteration: Slight alteration to unidentified material along cracks.

* With SrO calculated as CaO and K₂O presumed to be present as potash feldspar in solid solution.

REFERENCES TO CHEMICAL ANALYSES OF SAMPLES IN TABLE 2

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- (5) KRACEK, F. C., AND NEUVONEN, K. J. (1952), Thermochemistry of plagioclase and alkali feldspars: *Am. Jour. Sci.*, Bowen volume, 293–318.
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- (7) HOWIE, R. A. (1954–55), The geochemistry of the charnockite series of Madras, India: *Trans. Roy. Soc. Edin.*, **62**, (Part III, No. 18), 725–768.
- (8) TABLE 3 of this paper.
- (9) MILLER, F. S. (1935), Anorthite from California: *Am. Mineral.*, **20**, 139–146.
- (10) SUBRAMANIAM, A. P. (1956), Mineralogy and petrology of the Sittampundi complex, Salem District, Madras State, India: *Bull. Geol. Soc. Am.*, **67**, 317–390.

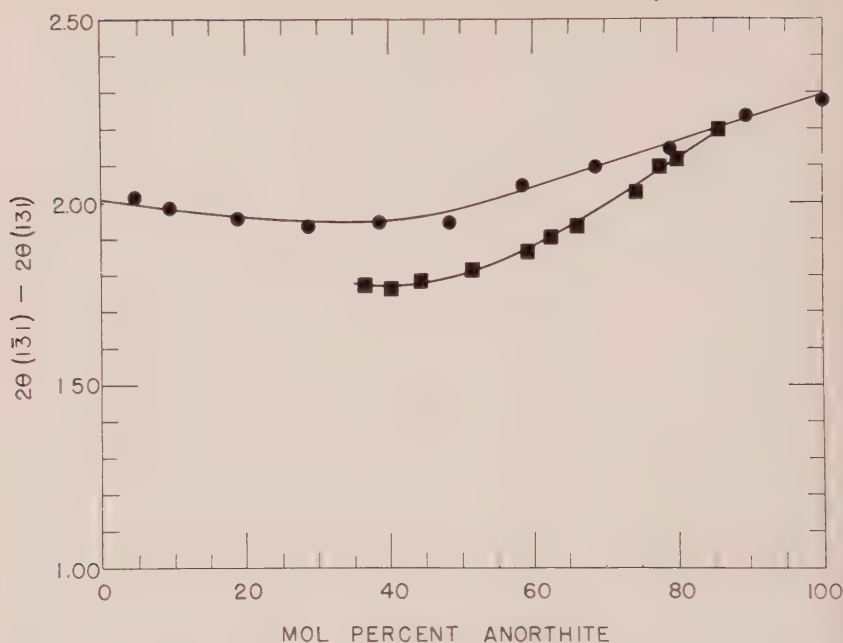


FIG. 2. Variation of $2\theta (1\bar{3}1) - 2\theta (131)$ with composition in plagioclases synthesized in the dry way (circles) and in plagioclases from thick stratiform mafic intrusions (squares).

from some of the same intrusions and avoids the use of the term "low-temperature plagioclases," which has yet to be defined.

The curves for the plagioclases synthesized in the dry way and for the plagioclases of the Bushveld type will now be used as a basis for comparison with the other plagioclases which were studied. The $(1\bar{3}1) - (131)$ separations for all the other plagioclases are plotted in Fig. 3, in which the curves of Fig. 2 are reproduced as full lines. The dashed line is representative of the studied samples of sodic plagioclases from pegmatites and granites (denoted by X's). The curve must be regarded as tentative, because there is some doubt as to the existence of homogeneous plagioclases of composition $An 6 \pm$ to $An 17 \pm$ in rocks formed at low temperatures or slowly cooled from higher temperatures.* If there is no

* Laves (1954) has shown that in the composition range $An 6$ to $An 17$ all the plagioclases which he studied from pegmatites and granites consist of two submicroscopically discrete phases. J. V. Smith (1956) states that the phases may or may not be resolved in powder diffraction patterns; if the phases are resolved, reflections representing only one phase may be mistakenly measured as reflections representing plagioclase of the bulk composition of the sample; if the phases are not resolved, peaks in powder patterns may be too broad to be measurable, as in the case of our sample number 2(10)($An 11.0$). Two of the samples represented in Fig. 3, numbers 3(73)($An 15.4$) and 4(156)($An 15.7$), were

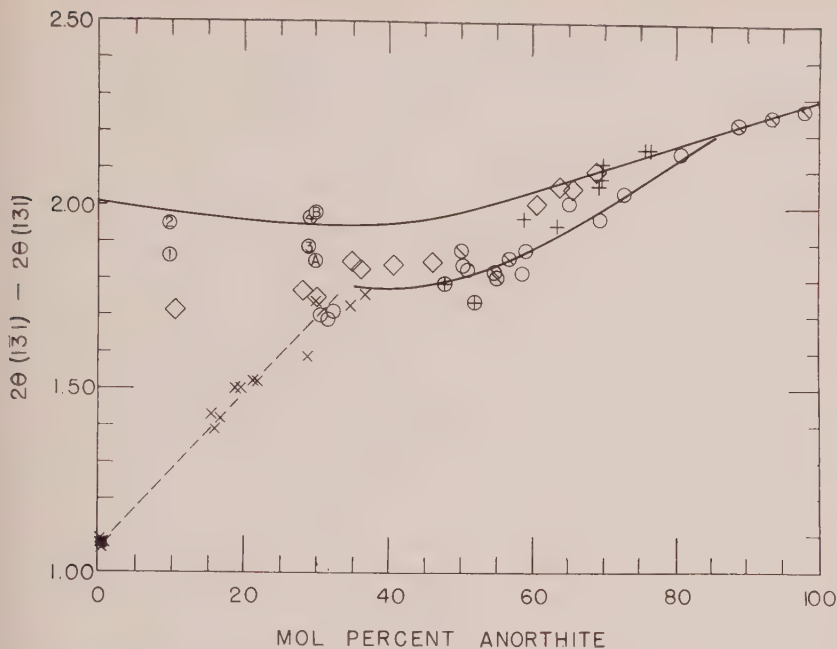


FIG. 3. Curves in full lines are the curves of Fig. 2. Symbols represent $2\theta(1\bar{3}1) - 2\theta(131)$ versus composition for plagioclases of the following origins:

- × from pegmatites and granites
- ⊙ from metamorphic rocks
- ◇ from volcanic rocks
- + from anorthositic masses near the tops of gabbroic sills, northern Minnesota
- ⊕ from Adirondack-type anorthosite massifs
- from miscellaneous rocks, details of occurrence not known
- ① and ③ synthesized from glass at 640° C. and 10,000 bars water pressure
- ② and ④ synthesized from crystalline material at 640° C. and 10,000 bars water pressure
- Ⓐ natural plagioclase from pegmatite heated for 9 hours at 1122° C.
- Ⓑ natural plagioclase from pegmatite heated for 24 hours at 1140° C.

real curve in this composition range, considerable uncertainty must be attached to the portions of the curve from An 0 to An 6 and from An 17 to An 35, because the slope of these portions depends to a large extent on the assumed validity of the projection of the curve through the An 6 to An 17 region.

studied by Laves (1954) and are known to consist of two phases. The two phases were not resolved in our powder patterns, and, since the values for the samples fall close to the dashed line in Fig. 3, the separation of the unresolved composite peaks is apparently representative of plagioclase of the bulk composition of the samples.

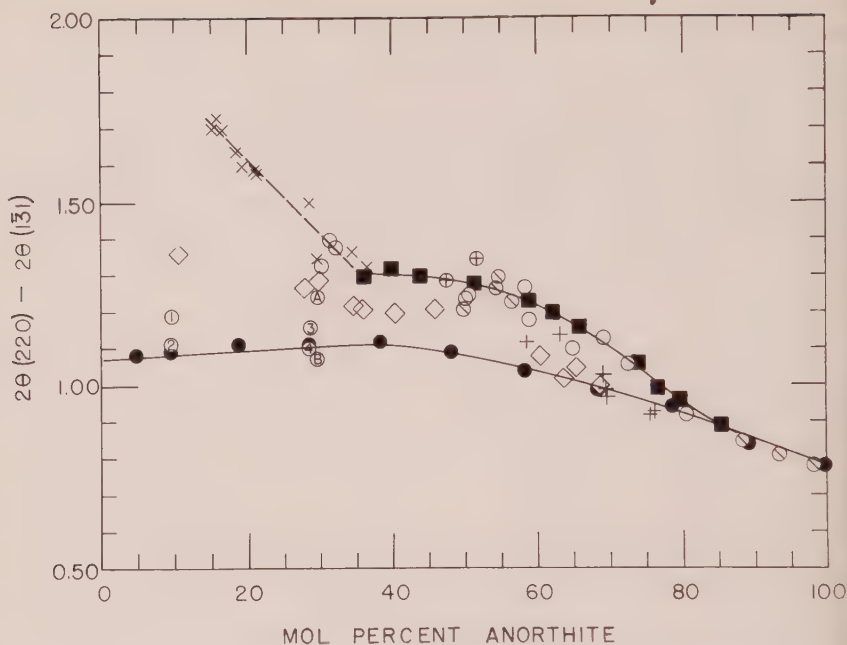


FIG. 4. Variation of $2\theta(220) - 2\theta(131)$ with composition for plagioclases synthesized in the dry way (closed circles) and plagioclases from thick stratiform mafic intrusions (closed squares). Other symbols are the same as in Fig. 3.

In the composition range An 30 to An 80, the large scatter of the points representing natural plagioclases is to be noted. Most of the scatter is due to the fact that the values for plagioclases from volcanic rocks and from anorthositic masses in thin gabbroic sills are intermediate between the curve for the plagioclases synthesized in the dry way and the curve for the Bushveld-type plagioclases; they approach the curve for the plagioclases synthesized in the dry way in the composition range An 65 to An 75. This presumably means that these plagioclases are "frozen" in somewhat higher temperature states than those represented by the Bushveld-type plagioclases, probably as a result of the more rapid cooling of the small extrusive and hypabyssal bodies in which they occur. However, the values obtained for some other samples are not readily explainable in terms of cooling rates. For instance, sample number C41 (An 50) is from a highly metamorphosed gabbro in a gneiss terrane in India (Subramaniam, 1956); the $(131) - (131)$ separation is significantly greater (i.e., tending toward "higher temperature" values) than that for Bushveld-type plagioclase of the same composition, which is not to be expected if the rate of cooling is the chief factor controlling the variation. Again, sample number KN6 (An 51.9) is from an Adirondack-type

anorthosite massif at Isle of Paul, Labrador (Kracek and Neuvonen, 1952); the $(\bar{1}\bar{3}1)-(131)$ separation is significantly smaller than that for Bushveld-type plagioclase of the same composition, suggesting that under certain (unspecified) conditions plagioclases may attain states of inversion which are apparently representative of lower temperatures than are the states attained by the Bushveld-type plagioclases. These isolated observations serve to point out the fact that the evidence of the state of inversion of a plagioclase afforded by x -ray parameters may be difficult to explain in terms of the geological evidence; the obvious conclusion is that more must be learned of the x -ray parameters of plagioclases from various geological environments.

In the composition range An 85 to An 100, there is no measureable difference between the $(\bar{1}\bar{3}1)-(131)$ separations for the plagioclases synthesized in the dry way and for the natural plagioclases which were studied, namely one Bushveld-type plagioclase and three from metamorphic rocks.

In order to discover whether similar relations would have resulted from measurements of other reflection separations, the $(220)-(\bar{1}\bar{3}1)$, $(\bar{1}\bar{3}2)-(24\bar{1})$, and $(\bar{1}\bar{3}2)-(\bar{2}41)$ separations were also measured. Figure 4 is a plot of all measurements made of the $(220)-(\bar{1}\bar{3}1)$ separation. A comparison with Figs. 2 and 3 will show that the relations are almost identical (although the relative positions of the curves are inverted). Closely similar results were also obtained from the $(\bar{1}\bar{3}2)-(24\bar{1})$ and $(\bar{1}\bar{3}2)-(\bar{2}41)$ separations.

The variation with composition of the F - G separation of Goodyear and Duffin (1954) appears to be fundamentally different from the variation of the $(\bar{1}\bar{3}1)-(131)$ separation. In attempting to measure the F - G separation in Geiger counter powder patterns, the writers found that both reflections are weak, and that the F reflection is not resolved from neighboring reflections. J. V. Smith (1956, p. 66) makes the following statement: "The F and G reflections of Goodyear and Duffin have the following indices: G , $(20\bar{4})$; F , probably mainly $(04\bar{3})$ but includes other reflections as well. Diffractometer records of reflection F often show a complex structure and it is doubtful whether it is suitable for measurement." Since the F - G separation could not be measured with an accuracy comparable to the other separations, its variation was not studied by the writers.

HEATED NATURAL PLAGIOCLASES AND PLAGIOCLASES SYNTHESIZED HYDROTHERMALLY

Tuttle and Bowen (1950) found that the values of x -ray parameters of natural plagioclases are changed to values similar to those of synthetic plagioclases by prolonged heating at temperatures near the melting

points, and that in some cases intermediate values can be achieved. Goodyear and Duffin (1956) and J. V. Smith (1956) have confirmed and enlarged upon these results. In the present study, heating of pegmatite plagioclase *D638* (An 29.5) for nine hours at 1122° C. caused the reflection separations to change to values about halfway between the original values and those of plagioclase of the same composition synthesized in the dry way. Heating for 24 hours at 1140° C. caused a change to values similar to those of plagioclase synthesized in the dry way (see Figs. 3 and 4). These and the previously mentioned experiments demonstrate that the state of inversion of a plagioclase is in some way a function of temperature, but the inability to reverse the reactions accompanying changing temperature has to date hindered experimental studies of the equilibrium relations.

Preliminary experiments to investigate the nature of plagioclases synthesized hydrothermally have been carried out. Plagioclases of composition An 10 (wt. %) and An 30 (wt. %) were synthesized at 10,000 bars of water pressure and 640° C., a temperature which is slightly below the extrapolated solidus temperatures at this water pressure (Yoder, unpublished data on Ab-An-H₂O). For each composition, two different starting materials were used, one glass and the other crystalline plagioclase synthesized in the dry way. In each case, the plagioclase produced from the crystalline starting material has reflection separations nearly the same as the starting material, whereas the plagioclase produced from the glass starting material has reflection separations significantly closer to the reflection separations of natural plagioclase of the same composition from pegmatite (see Fig. 3). It is doubtful whether either product represents the modification of plagioclase which is in equilibrium at 640° C., but the results suggest the possibility that experiments involving long periods of crystallization in the presence of water at low temperatures may ultimately lead to an understanding of the equilibrium relations.

LACK OF CONTINUITY OF THE CURVES

As may be seen in Figs. 3 and 4, there is a marked break in slope between the curve for plagioclases from granites and pegmatites and the curve for Bushveld-type plagioclases around An 35; there is a less marked discontinuity between the curves for Bushveld-type plagioclases and metamorphic plagioclases at An 85–90. At about the same compositions, one of the writers (J. R. Smith, 1954) has found discontinuities in the optical property curves for plagioclases from the same environments. Single-crystal x-ray studies to date have not disclosed any discontinuous

change in the crystal structure of plagioclases near An 35, but rather a gradual disappearance in the An 20 to An 30 region of certain subsidiary reflections characteristic of more calcic plagioclases from low-temperature environments (Gay and Smith, 1955). Likewise, in the range An 80–90, there appears to be a gradual change from a body-centered to a primitive unit cell in plagioclases from low-temperature environments (Gay, 1954). Inasmuch as the relations in these apparently critical regions might be different for suites of plagioclase samples from different geological environments, no interpretation of the discontinuities can be given on the basis of the present restricted sampling.

USE OF REFLECTION SEPARATIONS FOR DETERMINATIVE PURPOSES

As previously stated, other workers have recently published several studies of the variation of reflection separations with composition and with thermal history in the plagioclase feldspars. *The applicability and the accuracy of determinative curves based on the variations have been overestimated by some of the workers*, largely because the plagioclases studied were too few to adequately sample the variations existing in natural plagioclases from various source rocks. The curves may be valid for the particular samples studied, but had different samples been studied, different curves would have resulted. For instance, Claisse (1950), after studying reflection separations in eight natural plagioclases of various origins, concludes that a plagioclase composition can be determined to an accuracy of 1% An with the use of his curves, regardless of the origin of the sample. Goodyear and Duffin (1954) subsequently measured the same reflection separations measured by Claisse, using different samples; their data indicate that Claisse's curves are incorrect, and should not be used for determinative purposes. To a lesser degree, Goodyear and Duffin's curves for plagioclases "of presumably low-temperature origin" (Goodyear and Duffin, 1954, p. 306) are in turn subject to limitations, mostly because of the small number of samples used, but partly because three of the samples presumed by them to be of low-temperature origin are transitional between Bushveld-type plagioclase and plagioclase synthesized in the dry way (Goodyear and Duffin's samples numbered 7, 8, and 9; the same samples as our numbers 17(52), 18(134), and KN5). From the present study of a large number of natural plagioclases of various origins, the following conclusions regarding the use of reflection separations for determinative purposes may be drawn:

(a) The distribution of the points plotted in Fig. 3 demonstrates that natural plagioclases do not fall into two unique series. Volcanic plagioclases do not appear to constitute a unique high-temperature series, but

rather to be in various states of inversion between a "maximum" high-temperature state and some undefined lower temperature state. Similarly, plagioclases which have been hitherto presumed to be of "low-temperature" origin do not all fall into a unique low-temperature series. This being the case, the composition of a plagioclase cannot be determined by comparing its reflection separations with the curves of the present study or with curves previously published by others, because there is no *a priori* way of knowing how closely a particular plagioclase is represented by any of the available curves.

(b) Reflection separations for Bushveld-type plagioclases fall on a well-defined curve (Figs. 2 and 4). This suggests the possibility that a reflection separation versus composition curve could be determined for any suite of plagioclases of closely similar origins and thermal histories; such a curve could then be used for determinations of composition of other plagioclases from the same suite in the composition ranges where the slope of the curve is great enough to attain the desired accuracy. Curves so determined should be used with discretion. For instance, it is possible that plagioclases in the border zones of an intrusive body would be represented by a curve different from that representing plagioclases from the central parts of the body.

(c) If the composition of a plagioclase is known, and if it is in the range An 0 to about An 75, an estimate of its state of inversion may be made by measuring the $(\bar{1}\bar{3}1)-(131)$ separation and comparing its value with Fig. 3. Little quantitative value can be placed on the estimate, because different reflection separations give somewhat different estimates of the degree of inversion, as may be seen by comparing the positions of the points representing volcanic plagioclases in Fig. 3 with the positions of the same points in Fig. 4. The interpretation of the state of inversion of a plagioclase is subject to uncertainty because of the lack of knowledge concerning the relative importance of the various factors which might influence it.

ACKNOWLEDGMENTS

Most of the chemically analyzed samples studied were available at the Geophysical Laboratory, having been previously used for other purposes. The writers are indebted to the collectors and contributors of the samples, whose names are listed in Table 2. J. F. Schairer of this Laboratory generously made his samples of synthetic plagioclases available for study. Much valuable information was gained from the manuscript of J. V. Smith's paper on "The powder patterns and lattice parameters of plagioclase feldspars," to which reference has been made throughout the text.

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NOTES AND NEWS

A TECHNIQUE FOR MODAL ANALYSES OF MEDIUM- AND COARSE-GRAINED (3-10 mm.) ROCKS*

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Representative modal analyses of rocks with an average grain size greater than 2 or 3 mm., and of rocks which contain large, irregularly distributed crystals, cannot be made from standard 1-1½ inch square thin sections. Rapid, moderately precise modes of many such rocks can be obtained by sawing and grinding or polishing a smooth surface on a hand specimen, etching and staining the surface to aid in mineral identification, applying dot pattern Zip-A-Tone to the surface, and making a point count with the aid of a magnifier. The method has been developed for obtaining modes of medium- and coarse-grained granitic rocks from the Sierra Nevada and subsilicic rocks from the Stillwater complex. Detailed techniques are presented for etching, staining, and counting rocks ranging in composition from granite to dunite, but the general method should be applicable to a wider variety of rock types.

The general method has four principal advantages: (1) a slabbed face can be conveniently cut and prepared large enough to give a representative determination of mineral proportions in most medium- and coarse-grained rocks; (2) point counts can be made considerably faster on many etched rock slabs than on thin sections; (3) modal percentages of only one or two minerals can be determined without counting all the points, and (4) the method eliminates the problem of holes in thin sections. Larsen and Miller (1935, p. 263) and Chayes (1954, p. 1238-1239) have pointed out that standard thin sections of coarse-grained rocks do not contain sufficient grains to provide suitable samples for modal analysis; however, rock slabs can be conveniently prepared that contain 16 times the area of a thin section. Point counting on etched and stained slabs is relatively rapid because most principal minerals are quickly recognized and because the mechanics of manipulation are simpler. Furthermore, the most abundant mineral constituent need not be counted: the total number of dots in the area to be counted can be calculated, the minor minerals can be counted, and the major constituent can be found by difference.

The method has three principal limitations: (1) minerals must be identifiable on rock slabs; (2) the method cannot be conveniently applied to rocks with an average grain size less than about 2-3 mm.; and, (3) some small grain sections are concealed by Zip-A-Tone dots. In Stillwater and Sierra Nevada plutonic rocks most minerals are readily iden-

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tifiable on slabs after etching and staining, but distinctions between orthopyroxene-clinopyroxene and biotite-hornblende are difficult. Representative modal analyses of most rocks with average grain sizes less than 3 mm. can be obtained from standard thin sections; application of the dot count method to fine-grained rocks for which standard thin section areas do not provide a representative sample is limited by the relative increase in the size of the dots with respect to the grains. Patterns with finer dots than those now available would reduce the problem of concealment of small grains.

A slab surface provides a better sample of a coarse-grained rock than a standard thin section, and the dot-count method is believed to provide a representative sample of the area counted. The overall accuracy of the method has, however, not been worked out in detail. The assumed theoretical precision is based on the concept that the Zip-A-Tone overlay is essentially a simultaneous projection of a point counter pattern over the rock surface, and, that as such, it should be subject to the same theoretical treatment proposed by Chayes (1949, p. 1-11, et seq.). In practice, it is generally assumed that a minimum area 100 times the area of the largest grain in the hand specimen provides a representative sample of a structureless plutonic rock (Larsen and Miller, 1935, p. 271), but a larger area is prepared and counted if there is doubt of the applicability of this ratio to the particular rock. It is further assumed that a minimum of 1,000 dot counts in such an area provides an adequate sample of the area. To test the accuracy of the latter assumption, repeated point counts were made on etched slabs with the dot pattern shifted one-half of the dot interval between analyses. The modal percentage of individual minerals was generally reproduced within 1 per cent and the maximum variation was 2 per cent. Analyses of the same slab areas using different density Zip-A-Tone dot patterns produced results within these same limits.

PREPARATION OF THE ROCK SLABS

A hand specimen is examined and the approximate area of the largest grain is computed; a saw cut is then made that will provide a surface at least 100 times the area of the largest grain. The surface is ground on a standard lap with 280 carborundum abrasive until cleared of saw marks. Further grinding and polishing do not materially improve results on granitic rocks, and in some such rocks further polishing is apparently the cause of an unsatisfactory etch on the plagioclase. In rocks containing orthopyroxene and/or olivine, however, mineral distinctions after etching are accentuated on more highly polished surfaces; slabs of these rocks are therefore further ground with 3F carborundum and 303 $\frac{1}{2}$

alundum abrasive on a steel lap, then polished with 303½ alundum on a canvas lap.

Optimum procedures for etching and staining rock surfaces for counting were found to be considerably different for rocks of different composition, and techniques for the suites investigated are therefore treated separately. Polished slabs of Stillwater peridotites, feldspathic pyroxenites, and pyroxene gabbros are immersed in concentrated HF acid at room temperature for 1½ minutes, drained, dipped in water to neutralize the acid, and blown dry with compressed air. On the dry-etched surface plagioclase is chalky-white; olivine is dull gray; orthopyroxene, unaffected by the HF bath, is lustrous deep brown; clinopyroxene is a dull gray brown. In rocks containing both olivine and clinopyroxene distinction is aided by next immersing the slab in a 0.5 N solution of K₂CrO₄, and again blowing dry with compressed air. The pyroxenes are unaffected by the stain, olivine is brownish yellow, and plagioclase canary yellow. Ground slabs of Sierra Nevada granitic rocks are fumed about 1 to 2 cm. above the surface of a concentrated HF bath at room temperature for 3 minutes, and allowed to dry. The dry slab is then submerged in a sodium cobaltinitrite solution (50 g. in 100 ml. water as suggested by Chayes (1952, p. 339) gives satisfactory results) for about 20 seconds, rinsed in a gentle flow of cold water, and blown dry with compressed air. The etched and dry rock surface has bright yellow K-feldspar, chalky-white plagioclase, clear quartz, green biotite, and black hornblende. Care must be taken during washing, staining, and drying to avoid contact with the etched surface to prevent flaking off the delicate coatings on K-feldspar, plagioclase, and olivine. It is important that specimens stained with cobaltinitrite be thoroughly washed; excess solution will work out of cracks and mask all feldspar with an orange stain.

To protect the delicate etched and stained surface of the slab, several coats of clear liquid plastic are sprayed on the surface. Unfortunately, a plastic veneer generally leads to loss of distinction between orthopyroxene and clinopyroxene and between biotite and hornblende. In many rocks which contain either of these pairs of minerals, they can be distinguished by habit or color, but in some rocks distinction after coating with plastic is impossible. Dot patterned Zip-A-Tone may be applied to the final plastic spray coat while the surface is wet, or the Zip-A-Tone may be put on the dry plastic coated surface by using a small amount of mineral oil as an adhesive.

MECHANICS OF COUNTING

Zip-A-Tone pattern no. 3, which has relatively fine dots spaced about 1½ mm. apart (289 dots per square inch), is convenient for systematic

point by point counting of slabs; but a finer adhesive dot pattern, such as Para-Tone Company's Contak DT-45 (2116 dots per square inch) is more suitable for slabs on which only one or two minor constituents need be counted. Slabs up to 3 inches square covered with Zip-A-Tone no. 3 can be counted in one setting under a two power magnifier with a large field size. Finer dot patterns must be counted with a binocular microscope, and this not only slows counting, but leads to errors in transferring from one field to the next. Counts are tabulated with a blood counter from which the 100 count lock has been removed so that a continuous count can be made. It is relatively easy to complete a traverse of 30-40 counts without looking up from the slab after the touch system on the counter is familiar. A line in black ink along one side of the Zip-A-Tone cover is helpful so that a pin scratch mark can be made to show what line of dots has just been counted, as it is necessary to continue each traverse to the end without looking away from the surface of the rock. Zip-A-Tone dots cover part of the rock and it is therefore helpful and somewhat more accurate to choose consistently the same point on the circumference of each dot for the count. In some of the nearly monomineralic rocks of the Stillwater complex, counts of a given area can be made on an etched slab in about one-tenth the time needed to count the same area in thin section with a mechanical stage adapted for point counting. In granites, a 4 square inch etched slab can be counted in 20 minutes, about half the time necessary to make a point count on a 1 square inch thin section. The time it takes to saw, grind, polish, etch, and stain a coarse-grained rock plus the time necessary to make a point count on a Zip-A-Tone-covered surface of 4 square inches is less than the time it would take to make standard point counts on the 3 or 4 thin sections necessary to cover a similar area.

The slab point-counting method permits a rapid, reasonably accurate modal analysis on most varieties of medium- and coarse-grained plutonic rocks. The method should also be applicable to some metamorphic rocks, to some porphyritic extrusives, and possibly to certain indurated sedimentary rocks, such as granule conglomerates or stained carbonate rocks.

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A TECHNIQUE FOR MODAL ANALYSES OF SOME FINE- AND MEDIUM-GRAINED (0.1–5 mm.) ROCKS¹

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INTRODUCTION

A note by Jackson and Ross (1956) describes a rapid method of modal analysis for rocks with grain sizes ranging from about 3 to 10 mm. In this paper, an analogous method of modal analysis is described which applies to the more commonly encountered rocks with grain sizes ranging from 0.1 to 5 mm. The method can be used to supplement, though not replace, the use of thin sections for obtaining quantitative bulk compositions of essentially structureless rocks.

APPLICATIONS OF METHOD

Any rock of suitable grain size can be analyzed by this method if the minerals to be counted are readily recognizable, or can be made so by etching or staining. The more commonly used etching and staining techniques are described by Twenhofel and Tyler (1941). Jackson and Ross give procedures for staining mafic and ultramafic rocks, and also modifications of the method of Gabriel and Cox (1929) of staining for potassium with sodium cobaltinitrite.

EQUIPMENT USED

A photograph of the set-up for point counting on rock slabs is shown in Fig. 1. The equipment consists of a binocular microscope modified by replacing the standard glass stage with a one-fourth inch thick sheet of plexiglass of the same dimensions. A standard point counter mechanical stage for petrographic microscopes is then fastened to the sheet. An ocular equipped with a cross hair reticule provides a reference point for counting. A cruder but less expensive reference point can be established by cementing a five-eighths inch square cover glass to the ocular reticule ring, placing a fine India ink dot in the center of the cover glass, and screwing the cover glass into the focal plane of the eye-piece. Counts can be recorded on a tabulator.

COUNTING PROCEDURE

The point count on stained slabs is carried out in exactly the same way as in customary thin section analysis, and is subject to the same theoretical treatment proposed by Chayes (1949). According to Larsen and

¹ Publication authorized by the Director of the United States Geological Survey.

Miller (1935), a minimum representative sampling of an essentially structureless rock should be at least 100 times the area of the largest grain in that rock but in practice a considerably larger area is commonly used. The coarsest grained rock to which this method is applicable is governed by the largest slab that can be handled on the mechanical stage. A standard mechanical stage can traverse 75 mm. in an "east-west" direction and 25 mm. in a "north-south" direction. The capacity of the mechanical



FIG. 1. Equipment used for modal analyses on rock slabs.

stage can be increased: (1) by cutting a section 75 mm. by 50 mm. and counting the south and north halves of the slab separately; (2) by counting both sides of a slab 75 mm. by 25 mm. and thicker than the maximum grain size of the rock or; (3) by combining both of these methods. This would extend the range to include fairly representative samples of rocks in which the largest grains are 6 mm. square; however, with these coarser grained rocks the method of modal analysis described by Jackson and Ross would probably be faster and more suitable. The minimum grain size that can be counted using this method is determined solely by the magnifying power of the microscope used and by the ability of the operator to distinguish between the minerals in the slab. With a microscope equipped with a 3 power objective and 15 power ocular the practical minimum grain size that could be conveniently counted was found to be approximately 0.1 mm. The staining techniques used can be sufficiently discriminative to stain selectively the very finest-grained minerals visible with the binocular microscope.

It was found in practice that approximately 1,000 point counts regu-

larly distributed over a rock slab constituted an adequate sampling of that slab. For slabs 25 mm. by 36 mm. of rocks with maximum grain size less than 3 mm., 10 to 12 traverses are made spaced 2 mm. apart. For larger slabs of coarser grain size the counts are regularly distributed by adjusting the spacing of traverses, and by counting alternate points. After a little practice, an operator, counting four constituents can make 1,000 counts in 15 to 20 minutes.

Experienced operators can reproduce the modal percentage of essential minerals in a slab to within one per cent of the total in successive runs. The problem of determining surface boundaries with thin sections is generally not encountered in the rock slabs because the point count is being made upon the opaque upper surface of the slab which is essentially a plane. A strong point of this method is that an operator can make a fair modal analysis if he is able to distinguish the colors of the minerals being counted. No knowledge of optical mineralogy is required. As an experiment, three persons with no knowledge of mineralogy or prior experience in microscopy each made approximately 1,700 counts on a sodium cobaltinitrite-stained slab of granodiorite having a maximum grain size of 4 mm. square and average grain size of about 2 mm. After less than 30 minutes instruction and practice, the constituents, plagioclase, quartz, potassium feldspar, and mafic minerals were counted with the following results:

TABLE 1. COUNTS FOR MODAL ANALYSES ON A STAINED SLAB OF GRANODIORITE
(Volume Per Cent)

Mineral	Minimum	Maximum	Average	Max. deviation	Author's count
Plagioclase	46.8	52.0	49.3	2.7	50.7
Quartz	29.5	30.0	29.7	0.3	29.2
Mafic minerals	12.9	16.4	14.6	1.8	13.5
Potassium feldspar	5.6	7.2	6.6	1.0	6.1

With a little practice features such as grain size, shape, relative relief, and cleavage, in addition to color, are also used to identify the minerals, and a considerably higher degree of accuracy can be attained.

CONCLUSIONS

Point counting on slabs permits rapid, fairly accurate modal analyses on rocks of grain sizes ranging from about 0.1 to 5 mm. in which the essential constituents can be individually recognized. Because large slabs can be cut and measured as readily as small ones, it is possible to obtain more representative sampling of medium-grained rocks than could

be done with ordinary thin sections. Furthermore, inasmuch as little cost is involved in cutting and staining the slabs, many analyses could be made to reduce errors of sampling and of imperfect mixing in a rock mass. Grain boundary estimation is generally made on a planar opaque surface; therefore, there is no accumulative error, as in thin section analysis, owing to the presence of colorless minerals over opaque or strongly colored grains. Binocular vision in making the counts markedly decreases eye strain and the possibility of errors due to operator fatigue. The entire operation of cutting slabs, staining, and counting, can be readily and economically performed by unskilled personnel.

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YTTRIA IN ZIRCON

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The isostructural relationship of xenotime (YPO_4) and zircon (ZrSiO_4) is well known (Vegard, (1)), and isomorphous replacement of zircon by xenotime is assumed to be a common phenomenon; however, little published information is available as to the amount of such substitution that occurs.

The present investigation is a reconnaissance of the yttria content of natural zircons. Fifteen specimens from various localities and environments have been analyzed in order to gain some insight into the distribution of xenotime in zircons.

Analyses were made using a semi-quantitative spectrographic technique in which the yttria content of one zircon, concentrated from North Carolina beach sand, was determined using the addition method outlined by Ahrens (2). Two determinations using Specpure Y_2O_3 and xenotime gave 2.4 and 2.3% Y_2O_3 , respectively, for this standard. The yttria content of other samples was then found by comparison with the standard. All samples were ground to -400 mesh, tamped into carbon

TABLE 1

Specimen	Locality	%Y ₂ O ₃
Twinned zircon	Renfrew, Ontario	2.5±0.2
Zircon	Fredericksvarn, Norway	3.0±0.5
Zircon	Warwick, N. Y.	2.8±0.2
Zircon in nepheline	Norway	2.9±0.1
Zircon in syenite	Fredericksvarn, Norway	2.4±0.2
Zircon, concentrated from beach sand	North Carolina	2.4±0.2
Zircon, malacon	Hitteroen, Norway	4.3±0.7
Zircon	Essex Co, N. Y.	2.5±0.3
Zircon	No. Burgess Twp., Lanark Co., Ontario	2.4±0.1
Zircon	St. Peters Dome, Pikes Peak, Colo.	2.2±0.2
Zircon	Buncombe, N. C.	1.9±0.1
Zircon, cyrtolite	New Ross, Nova Scotia	3.9±0.2
Zircon	Madagascar	1.6±0.1
Zircon	Grattan, Ontario	>1.5
Zircon	—unknown—	2.1±0.5

electrodes, and excited as the anode in a 3 ampere d.c. arc. Each sample was run three or more times. The spectral line Y3216 Å was used for all microphotometric work.

The analytical results are given in Table 1. The yttria content ranges from a minimum of 1.6% to a maximum in a malacon of 4.3%. The yttria content is lognormally distributed with the mode at about 2.5% Y₂O₃.

The value of 2.5% Y₂O₃ corresponds to the presence of about 4% of xenotime by weight, which may be taken as the expectable amount of replacement by xenotime that the average zircon experiences.

An attempt to beneficiate the xenotime by magnetic separation was

TABLE 2

Sample		% Y ₂ O ₃
Zircon from pegmatite, Rockingham Lake, Renfrew Co., Ont.	mag.	4.7±0.8
	non mag.	2.5±0.4
Zircon from pegmatite, Troopers Lake, Glamorgan Twp., Ont."	mag.	3.1±0.7
	non mag.	2.3±0.4
Zircon from syenite, on Rte. 54 near Chicotimi, P.Q.	mag. at 4°	2.5±0.3
	mag. at 3°	3.0±0.3
	mag. at 2°	2.3±0.4

unsuccessful. Three samples of zircon separated from granite were run through a Franz Isodamic Separator and the fractions analyzed. The results are tabulated in Table 2.

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HYPOGENE GOETHITE AT PEKO MINE, N.T., AUSTRALIA*

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The primary copper ore at the Peko mine, Tennant Creek, Northern Territory, Australia, contains about 9 per cent copper and 4.5 dw. gold per ton. It is associated with a lens of magnetite rock, and consists of remnants of the magnetite rock in varying stages of replacement by pyrite, chalcopyrite, pyrrhotite, marcasite and minor amounts of wolframite, cobaltite, (?)safflorite, sphalerite, galena, bismuthinite, native bismuth, matildite, tetrahedrite, native gold, hematite and goethite (Edwards, 1955). The gangue minerals include quartz, siderite and chlorite.

Three ore zones have been exposed in development. From 200 ft. to 270 ft. (vertical depth) the ore is intensely oxidized and consists essentially of cuprite and native copper with some residual chalcocite, pyrite and native bismuth. From 270 ft. to 315 ft. it consists largely of chalcocite and covellite with variable amounts of residual chalcopyrite, pyrite and other primary minerals. Below 315 ft. depth the ore consists of primary sulfides.

On the 400-ft. level, in a zone of high grade ore, there occur a number of ovoids, or near spherical, bodies of relatively coarse-grained, massive pyrite from 2 cm. to 15 cm. diameter, which interrupt the weak banding in the ore. The banding is marked by thin strings of residual magnetite crystals running through massive chalcopyrite, parallel to the bedding of the wall rocks. It continues undisturbed above and below, and on either side of each individual ovoid of pyrite.

The contacts of these pyritic ovoids with the chalcopyrite ore are marked by dark brownish-black rims. These dark rims are somewhat irregular in thickness and shape. They look like reaction rims, in that their width corresponds to the size of the particular pyritic ovoid, rang-

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ing from 1 to 2 mm. wide for 2 cm. ovoids, up to 10 to 15 mm. wide for larger ovoids (Fig. 1), and they enclose scattered residual crystals of pyrite.

The dark rims consist of goethite, quartz and siderite, the goethite predominating. The goethite occurs as more or less spherical radiating acicular growths (Fig. 2), which in polished sections are bluish-gray and anisotropic with reddish-brown internal reflections, and in thin section are translucent reddish-brown, pleochroic from red-brown to golden-brown, and anisotropic. The identification of the goethite was confirmed by microchemical tests and an x -ray powder pattern. The individual goethite needles are commonly minute—0.015 mm. \times 0.002 mm.—though some are larger.

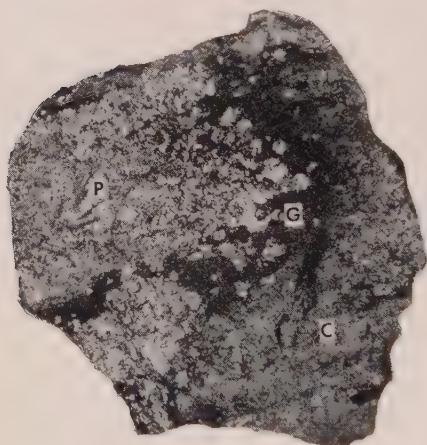


FIG. 1. Portion of a pyrite "ovoid," showing an irregular rim of dark goethite (G) separating the massive pyrite (P) from the enclosing chalcopyrite and magnetite (C). $\times 0.7$.

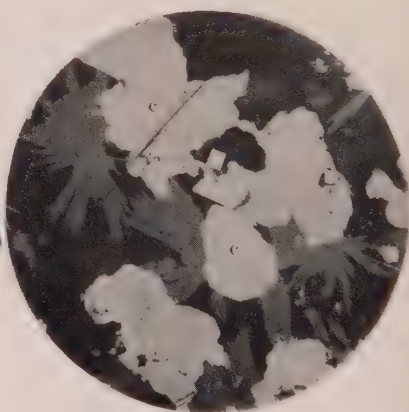


FIG. 2. Radial growths of goethite crystals (medium gray) moulded on chalcopyrite (c). The chalcopyrite encloses small corroded crystals of pyrite. Gangue is quartz (black). $\times 164$.

Polished sections of specimens from the outer margins of the goethite rims consist characteristically of clusters of goethite needles moulded on areas of chalcopyrite, which enclose small crystals of pyrite (Fig. 2). The goethite crystals project into the much coarser grains of quartz with which they are associated, and the chalcopyrite shows no evidence of corrosion, nor the least trace of oxidation.

Figure 3 shows a similar association of goethite, chalcopyrite and quartz, with clusters of minute crystals of pyrite fringing the central area of goethite.

Figure 4 shows a typical occurrence of goethite moulded on the edge of a crystal of pyrite, which is corroded where it is in contact with goethite or chalcopyrite. The goethite is also moulded on a grain of magnetite which shows no sign of oxidation, whereas in the zone of oxidation most magnetite in the Peko ore is more or less completely altered to martite.

Several of the pyrite ovoids were broken free from the enclosing chalcopyrite ore, which revealed that the goethite rims are not inter-connected, and have no extension through the ore away from the pyritic ovoids.

Similar goethite, less prominently developed, occurs in a zone of coarse pyrite forming the footwall of the lode and below the 400-ft. level. Here

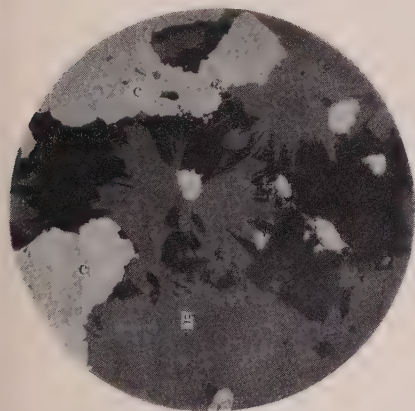


FIG. 3. Radiating clusters of goethite crystals (medium gray—*g*) moulded on chalcopyrite (*c*) and projecting into quartz (black). Clusters of minute pyrite crystals (white) occur on and in the margin of the central goethite cluster. $\times 164$.

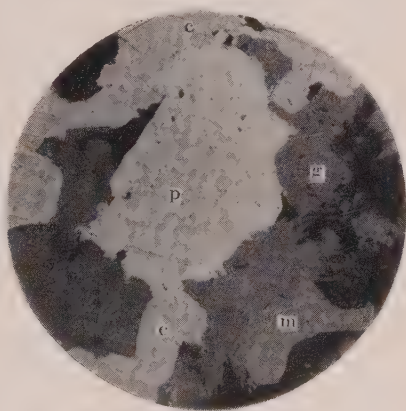


FIG. 4. Goethite (medium gray—*g*) moulded on pyrite (*p*), chalcopyrite (*c*) and magnetite (*m*). The pyrite is corroded at its contacts with goethite and chalcopyrite, but neither chalcopyrite nor magnetite shows any trace of oxidation. $\times 123$.

the goethite is associated with small rosettes of hematite, many of which are moulded on minute crystals of magnetite. Generally the radial growths of goethite needles are embedded in the quartz and siderite in the interstices of the hematite rosettes, but in places the goethite is moulded on the hematite, or intergrown with it. The magnetite crystals do not appear corroded, and show no trace of martitization. In places the hematite rosettes are moulded on areas of chalcopyrite, and these also show no traces of oxidation.

It is apparent that the goethite is not the product of supergene oxidation. It occurs well below the base of the zone of secondary sulfide enrichment, and its individual occurrences are isolated in completely

unoxidized ore. It is regarded therefore as a primary, hypogene mineral, deposited at a late stage of mineralization, along with quartz and siderite, as a result of a reaction between late ore solutions and earlier crystallized pyrite.

Since goethite converts to hematite above $125^{\circ}\text{C.} \pm 15^{\circ}$ under neutral conditions, and above $165^{\circ}\text{C.} \pm 5^{\circ}$ under alkaline conditions, independently of pressure (Smith and Kidd, 1949), it would appear that mineralization at Peko continued until the temperature fell below 165°C. , and possibly below 125°C. , in so far as the presence of marcasite points to acid conditions.

The occasional occurrence of wolframite, which appears to have been the earliest formed of the ore minerals, in conjunction with the presence of pyrrhotite in some abundance, indicates that mineralization began at a temperature of about 500°C. The presence of sphalerite studded with minute oriented ex-solution bodies of chalcopyrite points to a temperature of formation of $400\text{--}500^{\circ}\text{C.}$ for these minerals.

Presumably, therefore, mineralization at Peko extended over a temperature range of from 500°C. to below 165°C. and possibly below 125°C. This is comparable with the temperature range shown by a number of orebodies (Edwards, 1954, pp. 161–163).

If both ore and *country rock* at Peko cooled through 350°C. during the mineralization, then the mineralization was a long continuing process. This seems unlikely in view of the general preservation of fine-textured exsolution intergrowths of chalcopyrite in sphalerite in small areas of sphalerite throughout the primary ore.

The alternative interpretation is that the mineralizing fluids reached their locus of deposition at a temperature well above that of the adjacent *country rock*.

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COMMENTS ON TETRAHEDRAL HYDROXYLS

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In his note, "Antigorite: superlattice and structural formula," Zussman (1956) discusses, among other things, my comments (McConnell, 1954) on the results of Brindley and von Knorring (1954). Further clarification of these matters seems to be in order.

Commenting on my calculations, he states: "One should also consider the possibility that extra hydrogen atoms occur in the structure as $(\text{OH})^-$ replacing O^{--} ." It would seem obvious that this is exactly what the hypothesis involving tetrahedral hydroxyls calls for. The cogent matter is whether there is an equivalent decline in the number of silicon atoms, such that four hydrogen atoms proxy for each silicon atom and thus produce electrical neutrality.

Zussman points out (his formula (i)) that by omitting the 1.26 per cent of $\text{H}_2\text{O}(-)$ it is still possible to obtain tetrahedral hydroxyls. At the same time, however, almost half of the iron is interpreted as occurring in tetrahedral configuration. As he states, there are numerous results to be obtained, depending upon the diverse assumptions involved. My results assume that all of the constituents obtained on analysis occur in the lattice, *i.e.* no "impurities" are assumed to be present. Indeed, no impurities have been found by direct methods.

It is further shown by Zussman that if one assumes all of the iron atoms to have tetrahedral coordination and, simultaneously, if one assumes 2.3 per cent of the water liberated above 100°C . to be an "impurity," there is no need for concluding that hydrogens proxy for silicon atoms. Separately these assumptions seem dubious enough. Together they probably are completely untenable.

Although Zussman states that the case of ortho-antigorite is "not particularly suitable" for the purpose of indicating tetrahedral hydroxyls in phyllosilicates, it seems that he has considerably strengthened my brief arguments on the subject. He has considered an alternative possibility which involves far less plausible assumptions.

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McCONNELL, DUNCAN (1954), Ortho-antigorite and the tetrahedral configuration of hydroxyl ions: *Am. Mineral.*, **39**, 830-831.
ZUSSMAN, J. (1956), Antigorite: superlattice and structural formula: *Am. Mineral.*, **41**, 148-151.

STARKEYITE, A CORRECTION

OLIVER R. GRAWE, *Missouri School of Mines, Rolla, Missouri.*

Starkeyite¹ was described as a new mineral by the writer in 1945. It was found as a dull, white, powdery efflorescence on an altered mixture of pyrite and marcasite at the Starkey Mine in Madison County, Missouri. The country rock is a gray, granular glauconitic dolomite containing vugs lined with dolomite crystals. The dolomite rests upon a white friable sandstone and laps against a Precambrian felsite porphyry.

The association of the efflorescence with iron disulfide, qualitative tests for iron, and especially the agreement between the x-ray diffraction data for the new mineral and that for $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ led the writer to believe the composition of the mineral to be $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$. However, upon publication of data on the new mineral, Dr. Michael Fleischer² of the United States Geological Survey reported that Dr. W. T. Schaller had called his attention to the fact that the refractive index reported for starkeyite, 1.496, did not conform to the progression of indices for other hydrated iron sulfates when these are arranged in order of decreasing degree of hydration. The writer submitted a sample of the mineral to Dr. Fleischer for checking. As a result of further checking of the mineral at the United States Geological Survey, the refractive index reported by the writer was found to be correct. A partial analysis by the late Norman Davidson gave FeO 0.9, MgO 14.5, insol. in HCl 6.9 per cent. The powder diffraction patterns for $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ are nearly identical, which accounts for the writer's elementary error. On the basis of the analysis made at the United States Geological Survey, the composition of starkeyite should be $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$.

¹ Grawe, Oliver R. (1945), Pyrite deposits of Missouri: *Missouri Geological Survey and Water Resources*, pp. 209-210.

² Fleischer, Michael, Personal Communications, December 12, 1945 and January 24, 1946.

IMPROVED TECHNIQUES FOR STAINING POTASH FELDSPARS*

S. ROSENBLUM, *U. S. Geological Survey, Spokane, Washington.*†

INTRODUCTION

Chayes (1952) has described techniques for staining potash feldspar in thin sections so that it may be readily distinguished from quartz and untwinned plagioclase feldspar. His techniques were based upon earlier papers on the subject by Gabriel and Cox (1929) and Keith

* Publication authorized by the Director, U. S. Geological Survey.

† Now located at U. S. Geological Survey, Federal Center, Denver, Colorado.

(1939). This note describes modifications of Chayes' techniques that have been tested and used in a field office of the U. S. Geological Survey since March, 1954, with rapid and satisfactory results. Chayes' techniques were tried, using equipment described by him, but difficulties in manipulation of the equipment and uneven stains tended to discourage routine staining of thin sections. The following modifications of these techniques allow greater ease and control of the HF etch, and a simpler method of applying the cobaltinitrite stain. No attempt was made to test these modifications upon Na-rich potassium feldspars—the need for such tests never arose in our work—but we anticipate that the quality of the stain will be as poor as Chayes reported it to be.

THE HF ETCH

Chayes described a plastic butter dish cover, to hold HF acid, and a tray to support uncovered slides, face up, above the acid. When the tray is placed on plastic supports in the bath and covered by the bottom of the butter dish, fumes from the warmed HF rise around the slides and etch the minerals in the thin section for 30 seconds to prepare them for staining. We found that HF fumes, welling up and over the slides, etched the peripheries of the slides more than the centers, despite care in controlling the temperatures of the slides and the HF bath. A much more even HF etch is possible by placing slides face down over HF at room temperature (ca. 20° C.) in a small plastic fly-box (obtainable at most fishing-supply stores). Not only is the etch more easily controlled, but no backing is required on the slides since only the rock surfaces are exposed to HF fumes. Our present equipment is a 4-compartment box; each compartment is 1 inch by almost 1½ inches and ½ inch deep. The bottoms of 2 diagonal compartments are just covered with HF and two 1-inch by 2-inch slides (at room temperature) are etched at the same time for about 15 seconds. Similar results were achieved by H. W. Jaffe (1955, written communication) using an elongate lead dish upon which 6 or 8 thin sections were etched at one time.

An exposure of about 15 seconds was found to yield an evenly etched surface able to take any desired intensity of stain for thin sections: the intensity of the stain is controlled by the exposure to the staining solution. An etch of more than 30 seconds by this method is likely to cause pitting on the surface of potash feldspar and produce uneven, intense staining with many irregular clear areas in each grain. Thin sections should be thoroughly dry before etching to avoid solution of HF fumes in tiny water droplets and consequent over-etching. Before staining, HF fumes should be blown away or allowed to dissipate.

The acid may be stored in the fly-box by covering with the close-fitting

lid and placing it in a cool place, but in practice it has been poured back into a plastic bottle using a plastic funnel in order to reduce the danger of accidental spilling.

THE COBALTINITRITE STAIN

In place of Chayes' method of agitating slides (presumably one at a time) in the staining solution for 2 to 3 minutes, we stain 5 sections at a time in a Coplin jar filled with this same solution (ca. 60 grams sodium cobaltinitrite per 100 ml. water) for 15 to 20 seconds. Coplin jars, used by the medical profession for staining tissue sections, come provided with screw caps so that the staining solution may be stored in the jar when not in use. After staining, slides should be rinsed immediately in a gentle flow of cold water and allowed to dry thoroughly before covering.

Neither the rapidity of etching and staining nor the re-use of staining solution has caused any harm to any of the several hundred slides stained to date. A pale yellow color, just enough to distinguish potash feldspar from plagioclase feldspar and quartz rapidly in plane-polarized light, is the goal which has dictated the etch- and stain-periods given above. Notable success was achieved with numerous calcalkalic plutonic rocks and with the few metamorphic, arkosic, gabbroic, and syenitic rocks that were tried.

The clay minerals in altered rocks absorb the cobaltinitrite stain, but these may be distinguished by their unevenness in stain, their microcrystalline hummocky surfaces, and where potash feldspar is present for comparison, their different intensity of color.

Overstained thin sections may be restained by first gently rubbing the surface with "600 alundum" to remove the debris of the last etch and stain. According to Chayes (1955, written communication) the stain may also be removed with warm dilute HCl. After thoroughly drying the thin section, it may again be etched and stained as outlined above. Merely running warm water over the intensely stained surface will wash the stain out of the section, but in trying to lighten the stain by this means, we have had limited success. In most cases the stain is removed differentially and the result is blotchy; occasionally the result is usable.

REFERENCES

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GABRIEL, ALTON, AND COX, E. P. (1929), A staining method for quantitative determination of certain rock minerals: *Am. Mineral.*, **14**, 290-292.
KEITH, M. L. (1939), Selective staining to facilitate Rosiwal analysis, *Am. Mineral.*, **24**, 561-565.

CERITE FROM MOUNTAIN PASS, SAN BERNARDINO COUNTY,
CALIFORNIA*

JEWELL J. GLASS, HOWARD T. EVANS, JR., M. K. CARRON, AND
HARRY ROSE, JR., *U. S. Geological Survey, Washington, 25, D.C.*

The rare mineral cerite, a silicate of cerium and lanthanum, occurs with bastnaesite in one of the rare-earth-bearing veins of the Mountain Pass district, California. This district is 35 miles east of Baker, California. The deposits of rare-earth minerals are in a mineralized zone in shonkinite in an area of Precambrian metamorphic rocks. The minerals associated with cerite are: bastnaesite, barite, quartz, chalcedony, calcite, galena, and altered acmite.

Cerite from Mountain Pass is verona brown. The mineral occurs in massive form and in crystals that are pseudo-octahedral and range in size from 2 mm. to 7 mm. The mineral has a resinous luster, a hardness greater than 5, no observable cleavage, and gelatinizes in hot acid. Specific gravity as determined on the Berman microbalance is 4.78 ± 0.11 . The mineral is optically biaxial positive, with a very small optic angle. The indices of refraction are: $\alpha = 1.806$, $\beta = 1.806$, and $\gamma = 1.808$.

X-ray study of the crystallography of cerite by the Buerger precession method shows that the crystals are monoclinic with the following elements:

Space group: $I2/n(C_{2h}^6)$ or $In(C_2^4)$

Cell dimensions: $a = 17.81 \pm 0.09 \text{ \AA}$; $b = 10.85 \pm 0.06$; $c = 14.10 \pm 0.07$; $\beta = 109^\circ 10' \pm 10'$

Morphological elements: $a:b:c = 1.641:1:1.300$, $\beta = 109^\circ 10'$; $p_0' = 0.839$; $q_0' = 1.190$;
 $x_0' = 0.348$

Forms: a (100), d (011), e ($\bar{1}01$).

The forms listed above can be identified on the crystals. All forms are about equally developed, giving the crystals a pronounced pseudo-octahedral aspect.

Because of the large size of the unit cell, it is not possible to place any restrictions on the chemical formula. Calculations from the new chemical analysis suggest a possible formula for cerite to be $\text{Ce}_2\text{Ca}(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$. From optical, x-ray, and chemical evidence, the crystals contain some finely disseminated bastnaesite and possibly other impurities. Therefore, the validity of the proposed formula is inconclusive because of uncertainties due to corrections for these impurities.

A detailed description of cerite from Mountain Pass, California, is in preparation.

* Publication authorized by the Director, U. S. Geological Survey.

FIFTH NATIONAL CLAY CONFERENCE

The Fifth National Clay Conference will be held at the University of Illinois, Urbana, Ill., Oct. 8, 9 and 10, 1956. The conference is sponsored annually by the Clay Minerals Committee of the National Academy of Sciences—National Research Council, under the chairmanship of Prof. R. E. Grim of the University of Illinois.

PEACOCK MEMORIAL PRIZE, 1956

The Walker Mineralogical Club offers The Peacock Memorial Prize of One Hundred Dollars (\$100.00) for the best scientific paper on pure or applied mineralogy (including crystallography, mineralography, petrology, ore genesis, and geochemistry) submitted by any graduate student enrolled in a Canadian university, by a Canadian graduate student enrolled in any university, or by any graduate student on a Canadian subject. The paper will be accepted for competition up to two years after completion of the work even though the author may be no longer enrolled as a graduate student.

Full information on the conditions governing the presentation of this prize may be had by writing: The Secretary, Walker Mineralogical Club, 100 Queens Park, Toronto 5.

All papers for this year's competition must be in the Secretary's hands by October 31, 1956.

The following is a list of the current officers of the *American Crystallographic Association*:

President:	Dr. J. D. H. Donnay, Johns Hopkins University.
Vice-President:	Dr. Elizabeth A. Wood, Bell Telephone Laboratories.
Last Past President:	Dr. W. N. Lipscomb, University of Minnesota.
Treasurer: through 1958	Dr. George A. Jeffrey, University of Pittsburgh.
Secretary: through 1957	Dr. Jurg Waser, Rice Institute.

It is with deep regret that we record the death of Dr. William F. Foshag, head curator of the department of geology at the National Museum, Smithsonian Institution, Washington, D. C. Dr. Foshag died of a heart attack, May 21, 1956, at the age of 62. In 1940 he served as president of the Mineralogical Society of America and in 1953 he was the recipient of the Roebling Medal.

Professor Alexander Köhler of the Technischen Hochschule, Vienna, died Dec. 14, 1955, after a heart attack.

The Fourteenth Annual Pittsburgh Diffraction Conference will be held on Oct. 31, Nov. 1 and 2, 1956, at the Mellon Institute in Pittsburgh, Pennsylvania. This year it is the desire of the Conference Committee to emphasize (1) Small angle scattering, (2) High and low temperature diffraction studies, (3) Structural aspects of solid state physics, (4) Instrumentation and methods, and (5) Neutron diffraction. Titles of papers should be sent to the program chairman, Dr. A. Taylor, Westinghouse Research Laboratories, Beulah Road, Pittsburgh 35, Pa., before Sept. 1, 1956. Abstracts should be submitted by Sept. 20.

Erratum

An unfortunate misprint occurs on page 536 of the May-June issue; next to last line, "not" should be "now."

BOOK REVIEWS

PHASE DIAGRAMS FOR CERAMISTS, by ERNEST M. LEVIN, HOWARD F. MCMURDIE, AND F. P. HALL. The American Ceramic Society, Columbus, Ohio, 1956. 286 pages, 811 figures. Price \$10.00.

This is the latest in a series of five compilations of phase diagrams which, starting in 1933, have been published under the auspices of the American Ceramic Society. The last previous such effort, that of Hall and Insley in 1947 (with Supplement by McMurdie and Hall in 1949), is hereby brought up to date.

The present revision and expansion embodies a number of improvements over the previous edition. The general discussion has been enlarged from the eighteen pages of the 1947 version to thirty-four pages. The glossary of terms has been greatly extended and rearranged in alphabetical order. A useful addition is an annotated bibliography of about sixty selected titles covering the more important aspects of phase diagrams. An author index and a system index are provided as keys to the upwards of 800 diagrams included in the compilation. There is one invaluable source of phase equilibrium data which does not appear in the bibliography. This is the chapter entitled "Heterogenous Equilibria and Phase Diagrams," which has been a yearly feature of the Annual Review of Physical Chemistry since 1950.

Understandably, the authors considered it necessary to exclude some of the countless systems that have been investigated. This reviewer feels that exceptions might well have been made in the cases of such systems as: the carbon system (Goranson, *Scient. Monthly*, **51**, 524-535, 1940); recent additions to the $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ diagram (Segnit, *Am. J. Sci.*, **251**, 586-601, 1953); the $\text{Li}_2\text{O}-\text{BaO}-\text{SiO}_2$ system (Dietzel, Wickert, and Koppen, *Glastechnische Ber.*, **27**, 147-151, 1954); the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{ZrO}_2$ (Herold and Smothers, *J. Am. Ceram. Soc.*, **37**, 351-353, 1954); the systems $\text{CaO}-\text{MgO}-\text{Fe}_2\text{O}_3$, $\text{Mg}_2\text{SiO}_4-\text{MgO}-\text{Fe}_2\text{O}_3$, $\text{Ca}_2\text{SiO}_4-\text{MgO}-\text{MgO}-\text{Al}_2\text{O}_3$, and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3-\text{MgO}-\text{MgO} \cdot \text{Al}_2\text{O}_3$ (Rait, *Basic Refractories*, Interscience Publishers, 1950); six different melilite solid solution systems (Nurse and Midgley, *J. Iron and Steel Inst.*, **174**, 121-131, 1953); the system $\text{Na}_2\text{O}-\text{V}_2\text{O}_5$ (Canneri, *Gaz. Chim. Ital.*, **58**, 6-25, 1928); the system $\text{CaO}-\text{V}_2\text{O}_5$ (Morozov, *Metallurgie*, **13**, 21-28, 1938); and the system $\text{CaSiO}_3-\text{Ca}_2\text{Al}_2\text{SiO}_7-\text{NaAlSiO}_4$ (Juan, *J. Geol.*, **58**, 1-15, 1950).

In view of the inclusion of constant-percentage planes across certain quaternary systems (Figs. 458, 460, 483, 514, 515, 539, 540, and 541), one wonders at the exclusion of similar cross sections of the equally important $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system (Osborn, DeVries, Gee and Kraner, *J. Metals*, **6**, 3-15, 1954; Prince, *J. Am. Ceram. Soc.*, **37**, 402-408, 1954). Retention of the numerous iso fract diagrams, in the face of elimination of variation diagrams for optical properties of crystalline phases, is doubtless a concession to the needs of the glass technologist. The compilation reflects the rapidly expanding interest in hydrothermal systems, notably in those systems of most vital importance to the petrologist. A future similar increase in emphasis on high-pressure systems, both anhydrous and hydrous, is anticipated.

The compilers state that an attempt was made to eliminate outdated diagrams. In the opinion of this reviewer the following further eliminations could be justified. For the system $\text{BeO}-\text{Al}_2\text{O}_3$, Fig. 34 should be discarded. In the $\text{CaO}-\text{SiO}_2$ system Fig. 50 unnecessarily duplicates a portion of Fig. 49, and in the system $\text{Ti}-\text{TiO}_2$, Fig. 139 likewise duplicates a portion of Fig. 138. For the system $\text{CaO}-\text{TiO}_2$, Figs. 51 and 53 appear unnecessary. Of the three diagrams (Figs. 84, 85, and 86) for the system $\text{MgO}-\text{TiO}_2$, only Fig. 86 seems reliable. Figs. 119 and 129, for the systems $\text{Al}_2\text{O}_3-\text{TiO}_2$ and $\text{SiO}_2-\text{TiO}_2$ respectively, might well be

rejected as outdated. Two diagrams of the system $2\text{CaO} \cdot \text{SiO}_2\text{-}3\text{CaO} \cdot \text{P}_2\text{O}_5\text{-SiO}_2$, Figs. 591 and 592 are virtually identical. For the system $3\text{CaO} \cdot \text{P}_2\text{O}_5\text{-SiO}_2$, Fig. 596 seems to be preferred over Fig. 594. In the light of recent data (Figs. 142 and 143) for the system $\text{TiO}_2\text{-ZrO}_2$, Figs. 140 and 141 should almost certainly be rejected as untenable.

Admittedly, it was not the intent of the authors to evaluate the accuracy of any diagrams. However, in the course of this review some irregularities were noted which seem to merit at least passing comment. The diagram for the $\text{FeO-Al}_2\text{O}_3$ system (Fig. 73) shows a theoretically impossible rendition of the intersection of the corundum and hercynite liquidus curves. Fig. 88 for the system MgO-ZrO_2 is obviously in error, since it reverses the known temperature ranges of monoclinic and cubic zirconia. The diagrams for the systems $\text{BeO-MgO-Al}_2\text{O}_3$ (Fig. 255), $\text{BeO-Al}_2\text{O}_3\text{-ThO}_2$ (Fig. 258), and $\text{BeO-Al}_2\text{O}_3\text{-ZrO}_2$ (Fig. 260) do not incorporate the latest data on the system $\text{BeO-Al}_2\text{O}_3$ (Fig. 33). Diagrams for planes through the system $\text{CaO-MgO-(Al, Cr)}_2\text{O}_3\text{-SiO}_2$ (Figs. 539, 540, and 541) are unorthodox in assigning two phases to each primary field. In view of the probable inaccuracy of Fig. 140, the diagram for the system $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$ (Fig. 415) is questionable.

It was the policy of the authors to reproduce the phase diagrams essentially as they appeared in the original references cited beneath the diagrams. This has understandably resulted in wide deviation from uniformity in the presentation of details of the various diagrams. The reviewer would like to suggest that, for future editions of the compilation, the authors seriously consider a departure from this rigid policy. For well established binary diagrams, it should be a simple matter to insert the percentage compositions and the temperatures of eutectic and peritectic points, and the percentage compositions and the melting and inversion temperatures of end-members and intermediate compounds. The more important of the ternary diagrams might be accorded the treatment given to the $\text{Na}_2\text{O-CaO-SiO}_2$ diagram (Fig. 206). Such innovations would greatly increase the worth and convenience of the compilation.

This review has aimed at a critical appraisal with the dual purpose of providing some assistance to the prospective user of the book, and of stimulating the compilers to further improvement of an already outstanding piece of work. The authors and the American Ceramic Society are to be highly commended for this invaluable contribution to the ceramic literature. Like its predecessors, this latest edition is certain to prove an indispensable reference-work, not only for the ceramists for whom it was primarily intended, but also for mineralogists, petrologists, and all those concerned with nonmetallic mineral technology.

WILFRID R. FOSTER,
Ohio State University, Columbus, Ohio

MY HOBBY IS COLLECTING ROCKS AND MINERALS, by DAVID E. JENSEN, 120 pages; Hart Book Company, Inc., New York (1955). Price, \$2.95.

Among the duties of the professional mineralogist is advice and counsel to youngsters whose eyes have become opened to the fascination of minerals, and this frequently involves suggesting a book which will contain the answers to most questions an intelligent beginner is likely to ask, and yet not be too technical. The book under review fulfills these conditions admirably. Divided into 20 chapters it includes not merely descriptions of some 60 minerals, but also simple determinative tables, the classification of minerals and rocks, where to find rocks and minerals, collecting equipment, how to display and catalogue a collection, fun with minerals and blowpipe experiments, rock and mineral clubs, etc. The index has about 400 headings, each with an average of 2 or 3 references to the text. The book is beautifully illustrated, well printed on good paper, and strongly bound in cloth.

Mr. Jensen is Director of Geology of Ward's Natural Science Establishment, Rochester, New York, and in preparing this book he has notably continued the outstanding services

of the Establishment to American mineralogy. It is safe to say that the first steps of many boys and girls to a future career in mineralogy and geology will be guided by this book.

CHARLES MILTON,

U. S. Geological Survey, Washington 25, D. C.

STRUCTURE REPORTS FOR 1942-1944. Vol. 9. General Editor A. J. C. WILSON; Section Editors: N. C. BAENZIGER (Metals), L. M. BIJVOET (Inorganic Compounds), J. MONTEATH ROBERTSON (Organic Compounds). Published for the International Union of Crystallography. N. V. A. Oosthoek's Uitgevers Mij., Utrecht, Netherlands. viii+448 pp. (1955). Price 65.—Dutch florins, postpaid. Alternative: Polycrystal Book Service, 84 Livingston St., Brooklyn 1, N. Y. \$17.00.

Those who have already learned the value of the previous volumes of *Structure Reports* will welcome this latest volume. Those who are not familiar with this undertaking should know that the gap between the last volume of the old *Strukturbericht* (no. 7) and the new series of *Structure Reports* now lacks only Vol. 8 of being completely filled. This has been a long and tedious job for the editors and their associates, but they are performing a very valuable service.

LEWIS S. RAMSDELL,

University of Michigan, Ann Arbor, Michigan

NEW HAMPSHIRE MINES AND MINERAL LOCATIONS by PHILIP MORRILL.

Reproduced from typewritten manuscript, 64 pages, 16 maps (parts of U. S. Geol. Survey topographic sheets). For sale by Dillingham Natural History Museum, Naples Maine, at \$1.25. (1956 (?)).

This is a compendium of mineral localities in New Hampshire with listings of the various occurrences and the mineral species that have been found there. The pamphlets will be of considerable interest to mineral collectors, even though many of the minerals listed for some deposits have not been found there for many years. The localities are not evaluated in any way as present sources. The most valuable information is perhaps the pinpointing of many localities on maps in the rear.

E. WM. HEINRICH,

University of Michigan, Ann Arbor, Michigan

DIE BERGWIRTSCHAFT DER ERDE, by FERDINAND FRIEDENSBURG. 5th ed. 562 pp.+xvi. 49 figures. Ferdinand Enke Verlag, Hasenbergsteige 3 (14a), Stuttgart-W, Germany. 1956. DM 69.

Every attempt has been made, in this the fifth edition of this well known reference work, to incorporate up-to-date information on the mining industry of the world. As the subtitle indicates the book deals with the "ore deposits, mining industry, and mineral supplies of individual countries." A short general statement precedes the data for individual countries, which are presented alphabetically, "Aden to Vereinigte Staaten von Amerika"—154 entries, several embracing more than one country or geographic unit. The illustrations are sketch maps showing the location of ore deposits by means of appropriate symbols. Nearly every entry is accompanied by a table that presents data on mineral production, commonly through 1954. For each country a general statement on its mineral economy is followed by information on its mineral fuels, major metallic ores, rare metals, other metals, salts, and other minerals. The section on Germany is, of course, in notably greater detail than are those of other countries. One valuable feature is a attempt, even though necessarily much generalized, to evaluate the potential of many of the ore deposits or mineral resources.

Another is the inclusion of summaries on the political significance of the mineral industries and their functions in the economies of the countries. Numerous references close each section. A group of tables detailing production of the various individual metals and non-metallic substances (35 pages), usually for each year from 1945-1954 and broken down by countries, forms the concluding section of the book.

This is an exceedingly valuable work of reference to which all economic geologists should have ready access.

E. WM. HEINRICH,
University of Michigan, Ann Arbor, Michigan

GLANS EN GLOED UIT DONKERE DIEPTEN. by B. MIDDERIGH-BOKHORST (Glitter and Glow from dark depths.) 27X22 cm.; pp. 83, cardboard covers. The Hague (Holland), NILLMY, n.d. (1955).

Having learned of the success and interest shown in "Rockhound" clubs among teenagers in the U.S.A., the author, an accomplished artist, has produced a stimulating book for similar clubs in the Netherlands. Since the country has practically no rock outcrops, she confined herself to the description, illustration and identification of precious and semi-precious stones. Their characteristics are introduced through informal conversations between an elderly jeweller and teen-age boys and girls, in the course of which many interesting anecdotes and stories about famous gems are told. An outstanding feature is the collection of illustrations accompanying the text. This comprises reproductions in colors of some three dozen mineral species and varieties of natural and cut specimens after original paintings by the author. Many of them are strikingly beautiful. It is all the more remarkable that this excellent book sells for only fl. 2.80 (= 80¢ U.S.), the proceeds of which are donated entirely to an organization that cares for physically handicapped children.

M. W. SENSTIUS,
University of Michigan, Ann Arbor, Michigan

SOCIETY FOR EXPERIMENTAL STRESS ANALYSIS

1956 Annual Meeting
and Exhibit

October 31-November 1 and 2, 1956

Deshler-Hilton Hotel
Columbus 1, Ohio.

Further information regarding this event may be obtained by writing to:

Dr. W. M. Murray,
Secretary-Treasurer,
Society for Experimental Stress Analysis
Post Office Box 168,
Cambridge 39, Massachusetts

NEW MINERAL NAMES

Bursaite

RASIT TOLUN, A study on the concentration tests and beneficiation of the Uludağ tungsten ore. *Bull. Mineral Research and Exploration Inst. Turkey, Foreign Ed.*, No. 46-47, pp. 106-127 (1954-55) (in English).

In part of a large contact-metamorphic scheelite deposit, sphalerite is associated with tremolite, pyrite, calcite, garnet, quartz, scheelite, chalcopyrite, native Bi, and a new mineral. Analysis of a concentrate obtained by flotation and superpanner gave S 17.32, Pb 39.62, Bi 37.60, Fe 1.98, Zn 3.18; sum 99.70%, which is interpreted as pyrite 4.24, sphalerite 4.73, native Bi 5.43, and $Pb_5Bi_4S_{11}$ 85.30%. The mineral is metallic gray, prismatic, with "tabular cleavage." Under the ore microscope, it shows a high reflective power, is pleochroic, and anisotropic. It shows oblique extinction, hence is probably monoclinic. $G. > 6.2$.

X-ray powder data by D. A. Reelfs, Univ. Geneva, are given. The strongest lines are in Å. 2.88(10), 3.38(9), 2.05(9), 3.55(8), 2.15(8), 2.98(7).

The name is for Bursa Province, Turkey.

DISCUSSION: The x-ray data show many coincidences, but some discrepancies with the published data on two minerals of similar composition, cosalite ($Pb_2Bi_2S_5$)?, and kobellite [$Pb_2(Bi, Sb)_2S_5$]?. For example, Berry, *Univ. Toronto Studies, Geol. Ser. No. 44* (1940) lists 8 strong lines for cosalite, among which are lines at 2.84, 3.44, 2.06, 3.52, 2.17, and 3.02. Comparison with these two minerals must be made before bursaite can be accepted as a valid species.

MICHAEL FLEISCHER

Ferroselite

E. Z. BURYANOVA AND A. I. KOMKOV, A new mineral—ferroselite. *Doklady Akad. Nauk S.S.S.R.*, **105**, 812-813 (1955) (in Russian).

Prismatic crystals of the mineral are 0.2-0.5 mm. long and up to 0.1 mm. in cross-section. Color steel-gray to tin-white with a rose shade. Luster metallic. Streak black. Hardness 6-6.2 (microsclerometer). Very brittle.

The form {110} is prominent, commonly striated longitudinally. {011} was noted. Penetration twinning marked. Cleavage perfect parallel to the elongation. Laue, rotation, and oscillation photographs showed ferroselite to be orthorhombic, space group $Pnmm$ or $Pnn2$, $a = 4.78 \pm 0.02$, $b = 5.73 \pm 0.02$, $c = 3.57 \pm 0.02$ kX. These agree well with data on synthetic $FeSe_2$.

Microchemical tests showed the presence of Fe and Se, and the absence of S and Te. Fusibility $2\frac{1}{2}$ -3. In the closed tube, it gives a dark-red sublimate and the characteristic selenium odor. Magnetic after being heated. Dissolved by HNO_3 , only slightly by HCl and H_2SO_4 .

In reflected light ferroselite is rosy-cream with high reflecting power. Birefringence weak. Strongly anisotropic, showing greenish-gray to lilac colors under crossed nicols. Easily mistaken for marcasite or loellingite.

Ferroselite occurs with minor chalcopyrite and pyrite cementing sandstones and pelites in the Middle Devonian deposits of the Tuvinsk Autonomous Territory. Partly replaced on edges by a reddish-brown anisotropic mineral of high n and adamantine luster.

The name is for the composition, $FeSe_2$.

DISCUSSION: The name is unfortunate, because it is easily confused with that of the silicate ferrosillite.

M. F.

Galeite

A. PABST, D. L. SAWYER, AND GEORGE SWITZER, Galeite, a new mineral from Searles Lake, California. Abstract in *Bull. Geol. Soc. Am.*, **66**, 1658-1659 (1955).

Analysis gave NaCl 6.27, Na₂SO₄ 75.39, NaF 17.43, loss wt. at 120° 0.10; sum 99.19%, corresponding to Na₂SO₄ · Na(F, Cl). The mineral is therefore dimorphous with schairerite. It is rhombohedral; the space group is D_{3d}^1-P312/m or C_{3v}^2-P31m or D_{3d}^1-P312 ; the unit cell has a_0 12.17 ± 0.02, c_0 13.94 ± 0.02 Å, $Z=15$. Schairerite has a_0 12.17, c_0 19.29 Å, $Z=21$.

$G=2.605 \pm 0.005$ (detd.), 2.611 (calcd.). Optically uniaxial, positive, $\omega=1.447 \pm 0.002$, $\epsilon=1.449 \pm 0.002$, $\epsilon-\omega=0.002$ (direct measurement).

The mineral has been found only in drill cores. It occurs in small nodular aggregates of white crystals of maximum dimension 1 mm., embedded in clay and other salt minerals. In some nodules it is associated with gaylussite and northupite. The crystals are hexagonal, barrel-shaped, rarely tabular, and a rhombohedron with rho 66°25' is the most persistent form.

The name is for W. A. Gale, Director of Research of the American Potash and Chemical Corporation.

DISCUSSION: The name will cause confusion with halite (=galite in Russian).

M. F.

Garrelsite

CHARLES MILTON, J. M. AXELROD AND F. S. GRIMALDI, New mineral, garrelsite ($\text{Ba}_{.65}\text{Ca}_{.29}\text{Mg}_{.06}$)₄H₆Si₂B₆O₂₀, from the Green River formation, Utah.

Abstract in *Bull. Geol. Soc. Am.*, **66**, 1957 (1955).

Analysis (not given) on 27 mg. lead to the formula above. This is compared to those of datolite and bakerite.

Datolite	Ca ₄ B ₄	(SiO ₄ (OH)) ₄
Bakerite	Ca ₄ B ₄ (BO ₄)	(SiO ₄) ₃ (OH) ₃ · H ₂ O
Garrelsite	(Ba, Ca) ₄ B ₄ (BO ₄) ₂	(SiO ₄) ₂ (OH) ₂ · 2H ₂ O

The colorless crystals, a few mm. long, have a characteristic four-sided steep bipyramidal shape, formed by the prismatic faces (110) and ($\bar{1}\bar{1}0$), and the pyramidal faces (21 $\bar{1}$) and (2 $\bar{1}1$). The faces are striated by alternation of prism and pyramid. Monoclinic, space group C_4-Aa or C_{2h}^2-A2/a , $a=13.42$, $b=8.45$, $c=14.61$ Å, beta 114°19', $Z=4$. $G=3.68$ (measured), 3.73 (calcd.). Optically biaxial, neg., $\alpha=16.20$, $\beta=6.33$, $\gamma=1.640$ (all ± .003), $2V=72^\circ$, $\gamma=b$.

Garrelsite was found in a core from the Sun Oil Co. South Ouray No. 1 well, Uintah County, Utah, from a depth of 2139 to 2370 ft., in brown dolomitic shale containing nahcolite, shortite, searlesite, and microscopic wurtzite.

The name is for R. M. Garrels of Harvard University.

M. F.

NEW DATA

E. I. NEFEDOV, Neue Minerale. *Geologie* **4**, No. 5, 526-528 (1955).

Further brief notes are given on some of the minerals previously described (see *Am. Mineral.*, **40**, 551-552 (1955)).

Lodochnikovite

Shown by x-ray study to be orthorhombic with a_0 23.6 ± 0.1, b_0 17.1 ± 0.1, c_0 5.70 ± 0.05 kX. $Z=b$, $X=c$.

Volkovite

Now stated to contain approximately equal amounts of Ca and Sr.

Vladimirite

Monoclinic with a_0 5.80 ± 0.05 , b_0 10.17 ± 0.05 , c_0 22.7 ± 0.1 kX, β $82^\circ 41'$. α is 1.650, not 1.560.

Shubnikovite

The unit cell has a_0 14.02 ± 0.5 , b_0 14.05 ± 0.05 , c_0 $30 \pm kX$, β 90° . $Z=b$, $X=c$. $G.=3.38$.

M. F.

Leverrierite

A. SCHÜLLER AND H. GRASSMANN, *Leverrierit aus oberkarbonischen Kristallensteinen von St. Etienne, Frankreich. Chemie der Erde*, **17**, 233–240 (1955).

The name leverrierite was given by Termier in 1889 to a clay mineral occurring in vermicular aggregates in carbonaceous shales at several localities near St. Etienne, France. The early work, summarized in Dana's System, 6th Ed., p. 687, showed considerable variation in chemical composition. An analysis published by Termier, *Bull. soc. franc. min.*, **22**, 27–31 (1899), gave SiO_2 49.90, Al_2O_3 37.02, Fe_2O_3 3.65, MgO 0.30, CaO traces, K_2O 1.13, ignition loss 8.65; sum 100.65%. Some of the material had $\alpha=1.554$, $\gamma=1.582$, β very nearly identical with γ ; other samples including those originally described, had birefringences ranging from 0.008 to 0.030. In 1931, Ross and Kerr, *U. S. Geol. Survey Prof. Paper* **165-E**, found that material from the type locality had the optical properties of kaolinite ($\alpha=1.559$, $\beta=1.565$, $\gamma=1.566$) and also gave the x-ray diffraction pattern of kaolinite. They gave a photomicrograph of a vermicular crystal from St. Etienne and noted the presence of lenses of a second mineral along cleavage cracks.

On the basis of this work, the name leverrierite was generally dropped from the mineralogical literature as being synonymous with kaolinite.

In these papers published 1951–1953, A. Schüller and his co-workers described under the name leverrierite clays from several localities. Their use of the name was apparently based solely on the vermicular habit. They showed that its properties were those of a member of the illite group and pointed out that the name leverrierite had priority over the name illite.

In the present paper, material from Destival, St. Etienne is described. Analysis of a dried sample gave: SiO_2 48.99, TiO_2 0.25, Al_2O_3 37.64, FeO 0.35, CaO 0.72, MgO 0.57, K_2O 2.85, Na_2O 0.48, ignition loss (including 0.37% organic) 8.24; sum 100.09%. The original sample contained 0.95% H_2O^- . X-ray powder data and a *D.T.A.* curve agree with those given by members of the illite group. The conclusion is drawn that leverrierite was the first well-defined mineral of the illite group.

DISCUSSION: This new work proves that an illite clay, as well as kaolinite, occurs in the St. Etienne region. In spite of that, the previous descriptions of leverrierite from the type locality show clearly that what was described was mostly kaolinite with a slight admixture of an illite group mineral. It is therefore highly desirable that the term leverrierite be dropped completely. Its continued use has no advantage and only serves to cause confusion.

M. F.

Dillnite

JIRI KONTA, *Dillnit—ein spezifisches Tonmineral. Chemie der Erde*, **17**, 223–232 (1955).

The name dillnite was given in 1849 to a clay mineral later considered to be a mixture

of diaspore (known to occur in the deposit) with kaolinite. New study of type material from Banská Bela, Slovakia (= Dilln, near Schemnitz, Hungary, of old descriptions) shows the mineral to be a valid species. A new analysis gave: SiO_2 23.64, Al_2O_3 55.80, Fe_2O_3 0.04, CoO 0.12, MgO 0.28, $\text{H}_2\text{O} + 20.56$; sum 100.44%. This agrees well with 6 previous analyses and corresponds to $11 \text{ Al}_2\text{O}_3 \cdot 8 \text{ SiO}_2 \cdot 22$ (or 23) H_2O . Differential thermal analysis gave a strong endothermic reaction with a peak at 860°C . Dehydration study (heating 15 minutes at each temperature at 50° intervals) showed a loss of about 2% below 700° and complete dehydration at 800° .

The mineral occurs in gray-white earthy masses with conchoidal to even fracture. Inclusions of pyrite, diaspore, and fluorite have been found. Hardness about 2. $G = 2.675$. Triangular crystals have been observed (electron microscope photographs given), 2 to 15 microns in size. $n(\text{Na})$ 1.559 ± 0.001 , birefringence very weak, apparently less than that of kaolinite.

X-ray powder data are given. Spacings and intensities of the strongest lines are: 8.1, 10; 4.21, 10; 2.69, 10; 1.63, 9; 2.01, 7; 1.403, 7.

Discussion: The dehydration curve is remarkable for a mineral of such high water content. Further investigation is promised.

M. F.

The Fourteenth Annual Pittsburgh Diffraction Conference will be held on October 31, November 1 and 2, 1956, at the Mellon Institute in Pittsburgh, Pennsylvania.

This year it is the desire of the Conference Committee to emphasize

1. Small Angle Scattering
2. High and Low Temperature Diffraction Studies
3. Structural Aspects of Solid State Physics
4. Instrumentation and Methods
5. Neutron Diffraction

and papers on these subjects will be particularly welcome.

Titles of contributed papers should be sent to the Program Chairman, Dr. A. Taylor, Westinghouse Research Laboratories, Beulah Road, Pittsburgh 35, Pennsylvania, before September 1, 1956. Abstracts should be submitted by September 20.
